

Thiolate ligands effect on CO oxidation over CeO₂-supported Au₂₅(SR)₁₈ nanoclusters

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Introduction

Automobile emission control at low temperatures requires development of new efficient catalysts. Supported gold nanoparticles, extremely active for CO oxidation at ambient temperature, also exhibit promising low temperature performance in NO_x reduction. Thiolate ligand-protected gold nanoclusters, Au_n(SR)_m, with atomic precision and monodispersity have been recently attracted much attention due to their well-defined structures and excellent catalytic performances in various reactions.¹ The atomically precise Au nanoclusters are excellent model systems for understanding the structure-catalysis relationship and for designing more efficient Au-based catalysts for emission control. In this study, we explored the effect of thiolate ligands on the catalysis of CeO₂-rod supported Au₂₅(SR)₁₈ (SR = -SCH₂-CH₂-Ph) catalyst by using CO oxidation as a probe reaction. Reaction kinetic tests, *in situ* IR and X-ray absorption spectroscopy (XAFS), and density functional theory (DFT) were employed to understand how the thiolate ligands affect the activation of CO and O₂ and the reaction mechanism.

Materials and Methods

Au₂₅(SR)₁₈ nanoclusters were synthesized using the method reported previously.² Cerium oxide in a rod-like morphology was chosen as the support for Au₂₅(SR)₁₈ nanoclusters and synthesized using a hydrothermal method.³ CO oxidation kinetic study was carried out with a CO : O₂ ratio of 1 : 2 in both light-off and steady state modes on the catalyst (0.15 wt% Au) pretreated with O₂ at different temperatures (295 to 673 K). *In situ* IR coupled with CO adsorption and XAFS were conducted on the differently pretreated catalysts to probe both the nature of Au sites and the de-thiolation chemistry.

Results and Discussion

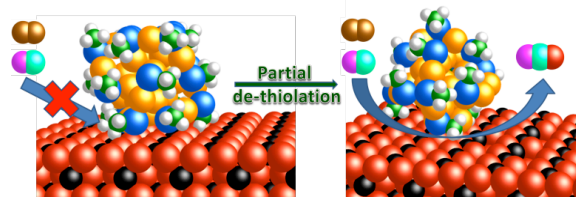
CO oxidation test on the different temperature pretreated Au₂₅(SR)₁₈/CeO₂-rod catalysts showed that no low temperature activity was observed on the as-synthesized sample. Low temperature activity was shown only when the sample was thermally treated at 423 K and above. The CO conversion was the highest on 523 K-pretreated sample. Higher temperature treatment leads to activity decline. The Arrhenius plots from CO oxidation with conversion below 30% show a similar activation energy, ~ 52 kJ/mol, for all the differently pretreated samples, indicating that CO oxidation follows a similar reaction mechanism. Also, the turnover frequency (TOF), based on the number of available Au sites for CO adsorption from IR study, was found similar on these samples.

The de-thiolation process occurring during the thermal treatment was followed by both *in situ* IR and extended X-ray absorption fine structure (EXAFS) spectroscopy. The as-

synthesized sample has intact Au₂₅(SR)₁₈ nanoclusters while 423 K treatment results in slight de-thiolation. Complete de-thiolation occurs at treatment temperature of 523 K without obvious Au size change. Higher temperature treatment leads to large structural change of the Au nanoclusters with slight size increase.

In situ IR coupled with CO adsorption provides information on the nature of Au sites on the differently de-thiolated Au₂₅(SR)₁₈/CeO₂-rod catalysts. There is no CO adsorption observed on the as-synthesized sample, indicating an intact, full thiolate protected Au₂₅ cluster cannot adsorb CO. This is supported by DFT calculation where the adsorption energy of CO on an intact Au₂₅(SR)₁₈ is negligible. Thermal treatment at 423 K and above partially removes thiolate ligands, creating coordinatively unsaturated Au sites that are able to adsorb CO. A majority of the Au sites is positively charged according to the frequency of adsorbed CO, consistent with *in situ* X-ray absorption near edge structure (XANES) measurements. The positive charge on Au nanoclusters likely originates from strong interaction between the Au nanoclusters and the ceria rods support.

CO oxidation mechanism on the Au₂₅(SR)₁₈/CeO₂-rod catalyst was investigated by isotopic labelling. Results from CO oxidation (CO + ¹⁶O₂) on ¹⁸O₂- and CO + ¹⁸O₂ on ¹⁶O₂-pretreated samples show that O₂-pretreatment does not create adsorbed oxygen species for low temperature CO oxidation. Instead, CO oxidation takes place predominantly at the interface among thiolate ligand, Au and CeO₂ on the partially de-thiolated Au₂₅(SR)₁₈/CeO₂-rod catalyst via a redox mechanism, i.e., CO is activated by accessible Au sites while CeO₂ activates O₂ and the lattice O participates in CO oxidation. Scheme 1 summarizes the main points of this study.



Scheme 1. Schematic representations of CO oxidation mechanism on intact and partially de-thiolated Au₂₅(SR)₁₈/CeO₂-rod catalysts.

Significance

This study clearly suggests that thiolate ligands act as a double-edged sword for the Au₂₅ nanoclusters for CO oxidation: they are needed to keep the structural integrity of Au₂₅ yet they also make the surface Au sites incapable in activating CO and catalyzing the subsequent CO oxidation reaction. The results here provide fundamental implications in how the ligand-protected Au nanoclusters can be further investigated and applied as effective catalysts for oxidation reactions involved in emission control catalysis.

References

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