

Understanding the Catalytic Role of Ligands in Supported Au_nR_m Nanoclusters for Gas Phase Reactions

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Introduction

Ligand-protected gold nanoclusters, Au_nR_m, with atomic precision and monodispersity have recently attracted much attention due to their well-defined structures and excellent catalytic performances in various reactions.¹ The atomically precise Au nanoclusters are ideal model systems for understanding the structure-catalysis relationship of Au-based nanocatalysts. Although general agreement has been reached on the role of the organic ligands in tuning reaction selectivity via electronic and steric effects, the role of the ligands on the catalytic activity is not consistent, especially for gas phase reactions. The goal of the current study is to elucidate how ligands may affect the catalytic properties of gold catalysts. We compared two different Au_nR_m nanoclusters supported on ceria for gas phase CO oxidation: thiolate ligands protected Au₂₅(SR)₁₈ (SR = -SCH₂-CH₂-Ph) with all surface Au atoms being coordinated and phosphine protected Au₂₂(L⁸)₆ (L⁸ = 1,8-bis(diphenylphosphino) octane) with coordination unsaturated (*cus*) Au atoms. Reaction kinetic tests, *in situ* IR and X-ray absorption spectroscopy (XAFS), and density functional theory (DFT) were employed to understand how the different ligands affect the activation of CO and O₂ and thus the reaction mechanisms.

Materials and Methods

Au₂₅(SR)₁₈ and Au₂₂(L⁸)₆ nanoclusters were synthesized using the method reported previously.^{2,3} These nanoclusters were loaded on ceria support via impregnation method. CO oxidation study was carried out in both light-off and steady state modes on the catalysts 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 ligands removal process.

Results and Discussion

CO oxidation test on the different temperature pretreated Au₂₅(SR)₁₈/CeO₂ catalysts shows no low temperature activity on the as-synthesized sample. Low temperature activity is observed only when the sample was thermally treated at 423 K and above. The CO conversion is the highest on 523 K-pretreated sample when the thiolate ligands are completely removed. In contrast, the as-synthesized Au₂₂(L⁸)₆/CeO₂ already shows considerable CO oxidation activity at low temperature. Thermal treatment of the catalyst at higher temperatures further increases the CO oxidation activity, a trend similar to that observed on Au₂₅(SR)₁₈/CeO₂.

The ligands removal 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 and Au₂₂(L⁸)₆ nanoclusters while 423 K treatment

results in slight ligands removal. Complete de-thiolation occurs at treatment temperature of 523 K without obvious Au₂₅ size change while the phosphine ligands are not completely removed even at 573 K although the Au₂₂ sample shows agglomeration. *In situ* IR coupled with CO adsorption provides information on the nature of Au sites on the different temperature treated Au nanoclusters. There is no CO adsorption observed on the as-synthesized Au₂₅(SR)₁₈/CeO₂ 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. In contrast, CO adsorption is apparent on the as-synthesized Au₂₂(L⁸)₆/CeO₂, due to the presence of *cus* Au sites in the intact Au₂₂(L⁸)₆. Thermal treatment at 423 K and above partially removes the ligands, creating *cus* Au sites on Au₂₅ and even more on Au₂₂ that are able to adsorb CO. The IR observation nicely supports the CO oxidation result of the two catalysts, strongly suggesting that *cus* Au sites are needed for Au nanoclusters to catalyze gas phase reactions. Interestingly, the oxidation state of Au sites as probed by CO is quite different for the two Au nanoclusters during the ligands removal process. At high ligands coverage, the Au sites are cationic and neutral for Au₂₅ and Au₂₂ nanoclusters, respectively. This can be attributed to the electron-withdrawing and electron-donating character of the thiol and phosphine ligands, respectively.

CO oxidation mechanism on the Au₂₅(SR)₁₈/CeO₂ catalyst was investigated in detail by isotopic labelling. Results from CO oxidation (CO + ¹⁶O₂) on ¹⁸O₂- and CO + ¹⁸O₂ on ¹⁶O₂- pretreated samples show that 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.⁴ A similar CO oxidation mechanism is expected for Au₂₂(L⁸)₆/CeO₂ catalyst.

Significance

This study clearly suggests that organic ligands can act as a double-edged sword for the Au_nR_m nanoclusters in gas phase reactions when the surface Au atoms are fully coordinated: they are needed to keep the structural integrity of the nanocluster, yet they also block the surface Au sites from activating reactants and catalyzing the subsequent reaction steps. Coordination unsaturated Au atoms are necessary for gas phase catalysis by the Au nanoclusters. The results here provide fundamental implications in how the ligand-protected Au nanoclusters can be further investigated and applied as effective catalysts.

References

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