

Reaction Mechanism for CO Oxidation over Iron Phosphate Supported Au Catalyst

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Introduction

Early work in catalysis by Au suggested that the use of reducible supports could lead to more active catalysts.¹ Although the differences in activities for reducible supports have been noted and their role in activating oxygen have been suggested^{2,3} there is little clear evidence that a Mars van Krevelen (redox) reaction mechanism plays a role in low temperature CO oxidation reactions. By proper synthesis, high activity can be achieved in Au catalysts supported on non-reducible supports.⁴ There are fewer investigations on non-oxide supported Au catalysts. We have explored metal phosphates (LaPO₄, FePO₄, AlPO₄, and others) as supports for Au catalysts.⁵ Au nanoparticles supported on certain metal phosphates showed not only high activity for CO oxidation and good thermal stability. The unique properties of this type of non-oxide supports may shed new light on the reaction mechanism associated with gold-based catalysts. We present evidence for two reaction pathways for CO oxidation on Au/FePO₄ at room temperature (rt): Mars-van Krevelen (redox) and direct (e.g. Langmuir-Hinshelwood or Eley-Rideal). Au species are differentiated and metallic Au catalyzes CO oxidation and assists the storage of active oxygen species on FePO₄.

Materials and Methods

Metal phosphate supports, MPO₄ (M=Al, Fe and La) were obtained commercially. Au catalysts were prepared by deposition-precipitation at pH 10. The precipitate was filtered, washed and dried at 40 °C. Most pre-treatment, chemisorption and reaction studies were carried out in a small volume DRIFTS reactor connected to a gas manifold with capabilities of rapid gas switching and for introducing gas pulses. A downstream mass spectrometer permitted correlating gas phase products with surface species determined by IR. Raman spectroscopy was carried out in a separate operando reactor and pulsed chemisorption was carried out in an Altamira AMI-200.

Results and Discussion

Room temperature (rt) CO adsorption was used to probe the nature of Au species on the fresh, dried Au/FePO₄ catalyst. Upon first introducing CO, adsorption occurs on cationic Au as indicated by two peaks at high stretching frequency, but with continued exposure these peaks decrease and a lower frequency peak increases. The latter is associated with adsorption on reduced Au increase and the distribution of peak intensities provides a measure of the Au oxidation state. Initial decrease of cationic Au is accompanied by CO₂ evolution. Subsequent rt exposure to O₂ does not restore the cationic Au, although once again CO₂ is evolved upon re-exposure to a CO stream. Therefore, an active oxygen species in Au/FePO₄ can be replenished by gas-phase O₂ at rt, but is not associated with reduction of cationic Au species. Three possible sources of the active oxygen species could be chemisorbed oxygen, oxygen from impurity Fe₂O₃ or lattice oxygen from Au/FePO₄. The absence of adsorbed oxygen was demonstrated 1) by isotopic analysis of CO₂ evolved following pre-treatment with ¹⁸O₂, and 2)

by Raman spectroscopy which failed to find evidence of adsorbed oxygen. Fe₂O₃ was not detected by XRD and in any case, tests on Au/Fe₂O₃ catalysts did not show similar behavior. Instead the source of active oxygen must be the FePO₄ as was confirmed by Raman and pulsed chemisorption experiments. Pulsed O₂ chemisorption proved the reducibility of the catalysts, and a Raman peak linked to reduction of the phosphate appears after rt CO exposure.

The rt redox property of FePO₄ in Au/FePO₄ is surprising because FePO₄ usually shows redox behavior only above 250°C in various oxidation and oxidative dehydrogenation reactions. Reduction of the FePO₄ must be facilitated by the presence of Au, since Au-free FePO₄ does not adsorb CO, evolve CO₂ or show evidence of reducibility below 200°C by pulsed chemisorption. It seems that the surface Au helps activate both CO and O₂ so that the FePO₄ support can undergo reduction by CO and reoxidation by O₂.

To determine the role of the redox pathway and the state of Au species during continuous CO oxidation reaction, ¹⁶O₂-treated Au/FePO₄ was used to catalyze CO oxidation by labeled ¹⁸O₂ at rt. Parallel growth of the IR bands due to gas phase C¹⁶O¹⁸O and adsorbed CO-Au⁰ (2119 cm⁻¹) suggests that the production of C¹⁶O¹⁸O takes place only after metallic Au is formed from the reduction of cationic Au by CO. This points to the positive catalytic role of metallic Au in rt CO oxidation on Au/FePO₄. Experiments formed over a H₂ pre-treated catalyst show IR bands and QMS signals due to C¹⁶O₂, C¹⁶O¹⁸O simultaneously from the very beginning of the reaction, suggesting that two reaction pathways exist, 1) a redox pathway in which FePO₄ supplies active O and 2) a direct pathway in which gas phase O₂ provides the active O occurring on metallic Au surface via either Langmuir-Hinshelwood or Eley-Rideal mechanism. This result is confirmed by gas switching between ¹⁶O₂ and ¹⁸O₂.

Significance

Our results demonstrate, for the first time, evidence for a redox mechanisms occurring on a non-oxide FePO₄ supported Au catalyst at low temperature. O₂ can be activated through incorporation as structural oxygen in FePO₄ with the assistance of gold, which opens a second pathway for CO oxidation. Both this redox mechanism and a direct mechanism are believed to occur in competition.

References:

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