

An Exploration of Catalytic Chemistry on Au/Ni(111)
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PROJECT SCOPE

This project explored the catalytic oxidation chemistry that can be effected on a Au/Ni(111) surface alloy. A Au/Ni(111) surface alloy is a Ni(111) surface on which less than 60% of the Ni atoms are replaced at random positions by Au atoms. The alloy is produced by vapor deposition of a small amount of Au onto Ni single crystals. The Au atoms do not result in an epitaxial Au overlayer or in the condensation of the Au into droplets. Instead, Au atoms displace and then replace Ni atoms on a Ni(111) surface, even though Au is immiscible in bulk Ni. The two dimensional structure of the clean Ni surface is preserved. This alloy is found to stabilize an adsorbed peroxo-like O₂ species that is shown to be the critical reactant in the low temperature catalytic oxidation of CO and that is suspected to be the critical reactant in other oxidation reactions. This investigation revealed a new, practically important catalyst for CO oxidation that has since been patented.

RESULTS

Nature of O₂ and O Binding on Au/Ni Surface Alloy

As part of our studies of the catalytic oxidation reactivity, we have carried out a detailed study of the interaction of O₂ with the Au/Ni(111) surface alloy. We find that the adsorption of O₂ is molecular at 77 K. This observation is in stark contrast to the adsorption of O₂ on Ni(111), which is dissociative even at 8 K. This observation is also in stark contrast to the interaction of O₂ with Au(111) because O₂ adsorbs neither molecularly nor dissociatively on Au(111) at or above 100 K. The addition of a small amount of Au to Ni lowers the Fermi level so that the overlap of the Ni 3d electrons with the π^* orbitals of O₂ is less than what it is on pure Ni. It is just enough less to stabilize O₂ from dissociation on the Au/Ni surface alloy but not so little as to preclude adsorption as on Au(111). Molecularly adsorbed O₂ on Au/Ni(111) is characterized by three distinct vibrational frequencies, 741 cm⁻¹, 852 cm⁻¹ and 963 cm⁻¹, as measured by high resolution electron energy loss spectroscopy, and are assigned to the vibration of the O=O bond of molecular oxygen adsorbed on the alloy with its bond axis largely parallel to the surface. Molecular oxygen so adsorbed is considered a peroxo (O₂⁻²) or superoxo (O₂⁻¹)

species. The three distinct O₂ vibrational frequencies reflect three distinct binding sites, where the vibrational frequency is inversely proportional to the binding energy. The three sites are populated sequentially as a function of Au coverage. The more strongly bound O₂, characterized by the lowest vibrational frequency of 741 cm⁻¹, is stabilized on the Au/Ni surface alloy at a low Au coverage, 0.25 ML. At 0.3 ML Au, a feature at 852 cm⁻¹ and a feature at 963 cm⁻¹ appear. The three features grow in intensity until a maximum intensity of the 741 cm⁻¹ feature is achieved at about 0.38 ML Au and a maximum intensity of the 852 cm⁻¹ and 963 cm⁻¹ features is achieved at about 0.45 ML Au. The intensity of all features then decreases as the Au coverage is increased and approaches zero at about 0.65 ML Au. The frequency of the 963 cm⁻¹ feature shifts up to about 1000 cm⁻¹ as the Au coverage increases from 0.45 ML to 0.65 ML.

A Monte Carlo simulation of the molecular O₂ coverage as a function of Au coverage was carried out to probe the site requirements for O₂ adsorption. The best agreement between the simulated and experimental O₂ coverage is observed when O₂ sits in a Ni atom bridge site of an ensemble of 6 Ni and 4 Au atoms of any hexagonal configuration. Molecular adsorption is blocked when an adsorbed O atom is within 5 Å of the bridge site. These high resolution vibrational spectra of molecularly adsorbed O₂ on the Au/Ni(111) surface alloy will serve as important benchmarks for the continued development of density functional theory for surface adsorbates.

The peroxo and superoxo species dissociate after heating the surface to 105-120 K as evidenced by the disappearance of their O=O stretch modes and the appearance of two features at 580 and 435 cm⁻¹, attributed to atomically adsorbed O. These features at 580 cm⁻¹ and 435 cm⁻¹ have the same frequency as observed for O atoms bound to Ni(111). Extensive detailed measurements have shown that about 10% of the O₂ does not dissociate but rather desorbs molecularly between 105-120 K.

Catalytic Oxidation of CO on a Au/Ni Surface Alloy

We have discovered that the peroxo and superoxo species stabilized on the Au/Ni(111) surface alloy efficiently oxidize CO at 70 K. The experiment is carried out in the following manner. Saturation coverage of molecular O₂ is adsorbed on the 0.44 ML Au/Ni surface alloy at 77 K. When a beam of thermal energy CO is directed at the O₂ covered Au/Ni(111) surface alloy held at 70 K, gas phase CO₂ is immediately produced. A control experiment demonstrates that no CO₂ is produced when the CO beam impinges on the crystal mount.

After exposure of the O₂-covered surface alloy at 70 K to CO, two C=O stretch vibrational modes are observed at 2170 and 2110 cm⁻¹, along with the Au/Ni-CO stretch mode at 420 cm⁻¹. The O=O modes at 852 cm⁻¹ and 963 cm⁻¹ are much reduced in

intensity, while the feature at 741 cm^{-1} has maintained its intensity. The decrease in intensities of the 852 cm^{-1} and 963 cm^{-1} features is interpreted to mean that most of the molecularly adsorbed O_2 has reacted with CO to form gas phase CO_2 . The product remaining from this reaction is an O atom adsorbed to Au, as evidenced by the appearance of a new feature at 660 cm^{-1} . The molecularly adsorbed O_2 that gives rise to the feature at 741 cm^{-1} appears not to react with CO.

This alloy surface covered with CO and some adsorbed O_2 is heated at 2 K/s while the partial pressures at masses 44 and 28 are monitored. Rapid production and desorption of CO_2 is clearly observed between $105\text{--}120\text{ K}$, along with CO desorption. Production of CO_2 in this temperature range occurs at the same temperature at which O_2 dissociates. This observation suggests that CO_2 formation occurs between CO and a "hot" O atom that has not yet equilibrated with the surface after bond dissociation. From 120 K to about 250 K , CO_2 is slowly produced by reaction of the adsorbed O atoms represented by 660 cm^{-1} mode and by the adsorbed O atoms that did not react immediately as a hot O atom upon O_2 dissociation.

Additional measurements of the CO_2 production at 77 K as a function of Au coverage show that CO_2 production correlates with molecular O_2 coverage (as measured by the intensity of the adsorbed peroxo species at 963 and 852 cm^{-1}), where the maximum CO_2 production and molecular O_2 coverage occurs at 0.44 ML Au .

These results demonstrate that Au/Ni(111) catalyzes the oxidation of CO at low temperature. A US patent has been awarded for the development and discovery of this catalyst. Clearly, substitution of a small number of Ni atoms on the Ni(111) surface by Au atoms has dramatically changed the Ni chemistry. The oxidation of CO on Ni has never been observed under UHV laboratory conditions, presumably because both the oxygen atom and CO are too strongly bound, and hence the barrier to their reaction is too large. Introduction of Au into the Ni lattice serves to weaken the bonds between oxygen and CO so as to allow the reaction to proceed. These results also imply that nanosize Au clusters are not a necessary requirement for low temperature CO oxidation in general. Rather, interaction of the Au atoms around the perimeter of the Au nanocluster with the transition metal of the oxide support likely provides the active sites that stabilize the adsorption of molecular O_2 that is necessary for the oxidation of CO.

PATENT

This investigation has resulted in an award of US patent No. 7,829,035 B2 on November 9, 2010 that is entitled Oxidation Catalyst to D. L. Lahr and S. T. Ceyer.

PUBLICATIONS

Catalyzed CO Oxidation at 70 K on an Extended Au/Ni Surface Alloy

D. L. Lahr and S. T. Ceyer, *J. Am. Chem. Soc.* **128**, 1800 (2006)

Stabilization of Molecular O₂ Adsorbed on a Au-Ni Surface Alloy

C. C. Leon, J. G. Lee, and S. T. Ceyer, in preparation, to be submitted to *J. Phys Chem.*

O₂ Dissociation on Au/Ni(111)

C. C. Leon, J. G. Lee, and S. T. Ceyer, in preparation, to be submitted to *J. Phys Chem.*

Oxidation of CO on a Au/Ni Surface Alloy

J. G. Lee, D. L. Lahr, J. D. Fischer, C. C. Leon and S. T. Ceyer, in preparation, to be submitted to *J. Phys Chem.*

Absolute Calibration of Au Coverage on Ni

C. C. Leon and S. T. Ceyer, in preparation

PH.D. THESES

Molecular Oxygen Adsorbates at a Au/Ni(111) Surface Alloy and Their Role in Catalytic CO Oxidation at 70 – 250 K, D. L. Lahr - June, 2006 – MIT

Adsorption of Molecular Oxygen on a Au/Ni(111) Alloy Surface and Its Oxidation of Co at 85 K, J. D. Fischer – September, 2010 – MIT

Catalytic Activity of Au/Ni Surface Alloys, C. C. Leon – expected June, 2012 - MIT