

dedicated to wendla

CO Oxidation over Gold

**Adsorption and Reaction of Oxygen, Carbon Monoxide,
and Carbon Dioxide on an Au(110)-(1×2) Surface**

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Previously published parts of this work

A. Refereed publications

1. J. M. Gottfried, K. J. Schmidt, S. L. M. Schroeder, K. Christmann, *Spontaneous and electron-induced adsorption of oxygen on Au(110)-(1×2)*, Surf. Sci. 511 (2002) 65-82.
2. J.M. Gottfried, N. Elghobashi, S.L.M. Schroeder, K. Christmann, *Oxidation of Gold by Oxygen-Ion Sputtering*, Surf. Sci. 523 (2002) 89-102.
3. J.M. Gottfried, K.J. Schmidt, S.L.M. Schroeder, K. Christmann, *Oxygen Chemisorption on Au(110)-(1×2). Part I: Thermal Desorption Measurements*, Surf. Sci. 525 (2003) 184-196.
4. J.M. Gottfried, K.J. Schmidt, S.L.M. Schroeder, K. Christmann, *Oxygen Chemisorption on Au(110)-(1×2). Part II: Spectroscopic and Reactive Thermal Desorption Measurements*, Surf. Sci. 525 (2003) 197-206.
5. J.M. Gottfried, K.J. Schmidt, S.L.M. Schroeder, K. Christmann, *Adsorption of Carbon Monoxide on Au(110)-(1×2)*, Surf. Sci., in press.
6. J.M. Gottfried and K. Christmann, *Adsorption of Carbon Dioxide on Au(110)-(1×2)*, Surf. Sci., in preparation.

B. Oral presentations

1. J.M. Gottfried, K.J. Schmidt, S.L.M. Schroeder, K. Christmann, *Adsorption von Methanol und Wasser auf Au(110)-(1×2)*, Verhandl. DPG (VI) 36 (2001) 1/358.
2. J.M. Gottfried, S.L.M. Schroeder, K. Christmann, *Chemisorption von Sauerstoff auf einer Goldoberfläche*, 101. Jahrestagung der Bunsen-Gesellschaft für Physikalische Chemie (Bunsen-Tagung), Potsdam 2002.
3. J.M. Gottfried, S.L.M. Schroeder, K. Christmann, *Oxidation einer Au(110)-(1×2)-Oberfläche*, Verhandl. DPG (VI) 37 (2002) 1/301.
4. J.M. Gottfried, K.J. Schmidt, K. Christmann, *Adsorption of Carbon Monoxide on Au(110)-(1×2)*, Verhandl. DPG (VI) 38 (2003) 5/411.
5. K.J. Schmidt, J.M. Gottfried, K. Christmann, *Adsorption of Krypton and Xenon on Au(110)-(1×2)*, Verhandl. DPG (VI) 38 (2003) 5/386.
6. J.M. Gottfried and K. Christmann, *CO Oxidation over Gold*, ECOSS 22, Prague 2003 (announced).

C. Poster presentations

1. J.M. Gottfried, K. Schmidt, K. Christmann, S.L.M. Schroeder, *Interaction of CO and CO₂ with clean and oxygen-precovered Au(110)-(1×2)*, ECOSS 18, Wien 1999.
2. J.M. Gottfried, K. Schmidt, R. Cames, S.L.M. Schroeder, K. Christmann, *Molecularly and atomically adsorbed oxygen on Au(110)-(1×2)*, ECOSS 18, Wien 1999.
3. J.M. Gottfried, K. Schmidt, R. Cames, S.L.M. Schroeder, K. Christmann, *Interaction of CO and CO₂ with clean and oxygen-precovered Au(110)-(1×2)*, BESSY-Jahrestreffen 1999.
4. J.M. Gottfried, K. Schmidt, R. Cames, S.L.M. Schroeder, K. Christmann, *Spontane und elektronenstimulierte Adsorption von Sauerstoff auf Au(110)-(1×2)*, Verhandl. DPG (VI) 35 (2000) 1/685.
5. J.M. Gottfried, K. Schmidt, A. Heiland, S.L.M. Schroeder, K. Christmann, *Wechselwirkung von CO und CO₂ mit einer reinen und sauerstoffvorbelegten Au(110)-(1×2)-Oberfläche*, Verhandl. DPG (VI) 35 (2000) 1/694.
6. J.M. Gottfried, K.J. Schmidt, S.L.M. Schroeder, K. Christmann, *Adsorption of Ethylene and Carbon Monoxide on Au(110)-(1×2)*, ECOSS 19, Madrid 2000.
7. J.M. Gottfried, K.J. Schmidt, S.L.M. Schroeder, K. Christmann, *Adsorption of Methanol and Water on Au(110)-(1×2): A Comparative Study*, ECOSS 19, Madrid 2000.
8. J.M. Gottfried, K.J. Schmidt, K. Christmann, *Adsorption und Reaktion von Kohlenmonoxid auf einer Goldoberfläche*, 102. Jahrestagung der Bunsen-Gesellschaft für Physikalische Chemie (Bunsen-Tagung), Kiel 2003 (announced).

D. Other publications

J.M. Gottfried, K. Schmidt, R. Cames, K. Christmann, S.L.M. Schroeder, *Atomically chemisorbed oxygen on Au(110)-(1×2)*, BESSY-Jahresbericht 1999.

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