BNL-99091-2013-CP

CO Oxidation at the Interface of Au Nanoclusters and the Stepped-CeO_2(111) Surface

Hyun You Kim and Graeme Henkelman

Presented at the New York Theoretical and Computational Chemistry Conference 2013
The Graduate Center, City University of New York, New York, NY
January 14, 2013

January 2013

Center for Functional Nanomaterials

Brookhaven National Laboratory

U.S. Department of Energy
Office of Science

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

This preprint is intended for publication in a journal or proceedings. Since changes may be made before publication, it may not be cited or reproduced without the author's permission.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

BNL-99091-2013-CP

Poster Presentation
New York Theoretical and Computational Chemistry Conference 2013
9th Floor, The Graduate Center, City University of New York, New York, NY
Jan. 14, 2013

CO Oxidation at the Interface of Au Nanoclusters and the Stepped-CeO_2(111) Surface[1]

Hyun You Kim and Graeme Henkelman

To reveal the richer chemistry of CO oxidation by CeO_2 supported Au Nanoclusters (NCs)/Nanoparticles, we design a Au_{12} supported on a stepped-CeO_2 model (Au/CeO_2-step) and study various kinds of CO oxidation mechanisms at the interface of the Au/CeO_2-step: oxygen spillover from the CeO_2 to the Au NCs;[2] CO oxidation by the O_2 bound to the Au-Ce^{3+} interface;[3] and CO oxidation by the Mars-van Krevelen (M-vK) mechanism.[4] DFT+U calculations show that lattice oxygen at the CeO_2 step edge oxidizes CO bound to Au NCs by the M-vK mechanism. CO_2 desorption determines the rate of CO oxidation and the vacancy formation energy (E_{vac}) is a reactivity descriptor for CO oxidation. The maximum E_{vac} that insures spontaneous CO_2 production is higher for the Au/CeO_2-step than the Au/CeO_2-surface suggesting that the CeO_2-step is a better supporting material than the CeO_2-surface for CO oxidation by the Au/CeO_2. Our results also suggest that for CO oxidation by Au NCs supported on nano- or meso-structured CeO_2, which is the case of industrial catalysts, the M-vK mechanism accounts for a large portion of the total activity.

(1) Kim, H. Y.; Henkelman, G. CO Oxidation at the Interface of Au Nanoclusters and the Stepped-CeO_2(111) Surface by the Mars–van Krevelen Mechanism. *J. Phys. Chem. Lett.* **2013**, *4*, 216-221.
(2) Guzman, J.; Carrettin, S.; Corma, A. Spectroscopic Evidence for the Supply of Reactive Oxygen during CO Oxidation Catalyzed by Gold Supported on Nanocrystalline CeO_2. *J. Am. Chem. Soc.* **2005**, *127*, 3286-3287.
(3) Kim, H. Y.; Lee, H. M.; Henkelman, G. CO Oxidation Mechanism on CeO_2-Supported Au Nanoparticles. *J. Am. Chem. Soc.* **2012**, *134*, 1560-1570.
(4) Kim, H. Y.; Henkelman, G. CO Oxidation at the Interface between Doped CeO_2 and Supported Au Nanoclusters. *J. Phys. Chem. Lett.* **2012**, *3*, 2194-2199.

Work supported in part by Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886 with theU.S. Department of Energy.

Dr. Hyun You Kim
Center for Functional Nanomaterials, Brookhaven National Laboratory

Professor Graeme Henkelman
Department of Chemistry and Biochemistry, University of Texas at Austin