



BNL-99863-2013-CP

***Understanding of catalytic behaviors of
TiO₂/CuO_x catalysts***

Hyun You Kim¹ and Ping Liu²

*¹ Center for Functional Nanomaterials, Brookhaven National Laboratory,
Upton, NY*

*² Chemistry Department, Brookhaven National Laboratory,
Upton, NY*

*Presented at the 246th American Chemical Society National Meeting and Exposition
Indianapolis, IN
September 8-12, 2013*

March 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.

Oral Presentation
246th ACS National Meeting & Exposition
Indianapolis, IN, September 8-12, 2013

Understanding of catalytic behaviors of TiO₂/CuO_x catalysts

Hyun You Kim and Ping Liu

Aiming to reveal the catalysis at the metal-oxide and oxide-oxide interfaces,^{1,2} the water-gas shift reaction (WGS, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) and CO oxidation ($2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$) at the interface of the Cu(111) and Cu₂O(111) supported TiO₂ clusters were studied based on DFT calculations,

Our DFT calculations showed that TiO₂/Cu(111) and TiO₂/Cu₂O (111) behave differently. TiO₂/Cu(111) was found to be more selective to catalyze the CO oxidation reaction, where a bifunctional effect is confirmed. Under the CO oxidation condition, O₂ interacts strongly with both Ti and Cu at the interface of TiO₂ and Cu(111) and the O-O bond cleavage is barrierless. The dissociated O atoms oxidize the CO adsorbed at Cu(111) efficiently. The WGS reaction on Cu(111) is slowed down by water dissociation. On depositing TiO₂ clusters, H₂O prefers to adsorb and dissociate easily at Ti ions to produce OH species. However, the facilitated water dissociation does not seem to help the WGS reaction. According to our calculations, CO is much more strongly bound at the interface of TiO₂ and Cu(111) than that on pure Cu(111), which hinders the reaction between CO and OH and therefore the overall WGS conversion. When Cu support is oxidized to Cu₂O, the TiO₂/Cu₂O (111) system favors H₂O adsorption and dissociation more significantly than CO adsorption, and the surface is likely to be saturated by OH species. Thus, the surface fraction of CO is minimized and the further oxidation via both WGS and CO oxidation is hindered.

Our results highlight the importance of the interface effects in multi-component catalysts, particularly as a means to tune the catalytic activity and selectivity. Such understanding is the key for the interface engineering in catalysis design.

- (1) Park, J. B.; Graciani, J.; Evans, J.; Stacchiola, D.; Ma, S.; Liu, P.; Nambu, A.; Sanz, J. F.; Hrbek, J.; Rodriguez, J. A., Controlling the Nature of Mixed-Metal Oxide Catalysts at the Nanometer Level: High Activity of Au/CeO_x/TiO₂(110) in the Water-Gas Shift Reaction. *Proc. Nat. Acad. Sci.* **2009**, *106*, 4975-4980.
- (2) Vidal, A. B.; Liu, P. Density functional study of water-gas shift reaction on M₃O_{3x}/Cu(111). *Phys. Chem. Chem. Phys.* **2012**, *14*, 16626-16632.

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

Dr. Hyun You Kim
Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY
11973, USA

Dr. Ping Liu
Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, USA