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## Catalysis Club of Philadelphia

Thursday September 20<sup>th</sup>, 2012

DoubleTree Hotel

4727 Concord Pike Wilmington, DE 19803

### Water Gas Shift over Industrial Cu Catalysts: A Mechanistic and Microkinetic Investigation

Rostam J. Madon

BASF Corporation, Iselin, NJ

**Social Hour: 5:30 PM**  
**Dinner: 6:30 PM**  
**Meeting: 7:30 PM**

**Members: \$35.00**

**Walk Ins & Non-members: \$40.00**

**Student & Retired Members: \$20.00**

#### **Menu**

**Herb Crusted Salmon** coated with a fresh herb crust aside duchess potatoes, bean medley & Dijon mustard sauce

**European Roasted Chicken**, whipped potatoes & Gorgonzola creamed spinach

**Vegetarian:** Hand Rolled Vegetable Lasagna stuffed with freshly Grilled Vegetables, Ricotta & Mozzarella Cheeses

**Vegan:** 5 oz. Phyllo stuffed with vegetables, served with roasted tomatoes

**Meal reservations** - Please notify your company representative or Jacob Weiner (jlweiner@udel.edu, phone: 302.831.2213) by **Thursday September 13<sup>th</sup>**.

Company Representatives – We would like to encourage you to make meal/meeting reservations to your company representative.

**Membership** - Dues for the 2012-13 season will be \$25.00 (\$5.00 for the local chapter and \$20.00 for the national club). Dues for students, post-docs and retirees will be \$10.00 (\$5.00 for local club and \$5.00 for national club).

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## Water Gas Shift over Industrial Cu Catalysts: A Mechanistic and Microkinetic Investigation

Rostam J. Madon

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### Abstract:

Low temperature water gas shift (LTS) is a commercially important reaction that takes place over a Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst. A large number of fundamental studies have been carried out for this reaction including investigations of the reaction mechanism as typified by Refs. [1-4]. In short, discussions have centered around (a) the redox mechanism in which adsorbed H<sub>2</sub>O is dissociated to O\* and OH\* and the O\* is removed via CO\* to form CO<sub>2</sub> – where \* is an active site, and (b) formate as a reactive intermediate. Recently, Gokhale et al. [5] using a DFT investigation of the LTS reaction on Cu(111) proposed a new mechanism that involves a reactive surface carboxyl. Our study is aimed at resolving which elementary steps best describe the catalytic cycle for the LTS reaction. To achieve this, we used the microkinetic modeling methodology pioneered by Dumesic [6], and analyzed our reactivity data using all elementary steps, including those that described the redox mechanism, the formate mechanism, and the carboxyl mechanism. Thus, we ensured that there was no bias towards any particular reactions to fit our data. We found the closed catalytic cycle for LTS on Cu consists of eight elementary steps that include the formation of COOH\*, and its reaction with OH\* to form CO<sub>2</sub>\* and H<sub>2</sub>O\*. The cycle does not include the reaction of CO<sub>2</sub>\* and H\* to form surface formate. However, this is an important side reaction, which ensures significant coverage of bidentate formate species on the Cu surface. Bidentate formate is a spectator species whose coverage increases with increasing pressure and decreases with increasing temperature. In summary, our investigation demonstrates that the redox and formate mechanisms are not relevant, and that the LTS catalytic cycle involves the formation and reaction of surface carboxyl. Several related aspects of the LTS reaction on Cu will also be discussed.

### References:

1. Ovesen, C. V., et al. *J. Catal.* **158**, (1996), 170.
2. Koryabkina, N. A. et al. *J. Catal.* **217**, (2003), 233.
3. Rhodes, C., Hutchings G.J., and Ward A.M. *Catal. Today* **23**, (1995), 43.
4. Herwijnen, T.V., and de Jong, W. A. *J. Catal.* **63**, (1980), 83 and 94.
5. Gokhale, A. A., Dumesic, J. A., and Mavrikakis, M. *J. Am. Chem. Soc.* **130**, (2008), 1402.
6. Dumesic, J. A., et al. "The Microkinetics of Heterogeneous Catalysis", American Chemical Society, Washington, D. C., 1993.

**Speaker Bio:**

Ross completed his undergraduate studies in chemical engineering at the University Department of Chemical Technology, Mumbai, India. He did his graduate work at Stanford University, obtaining his Ph.D. under the guidance of Professor Michel Boudart. After completing his post-doctoral work with Professor W. Keith Hall at the University of Wisconsin - Milwaukee, Ross joined Exxon Research and Engineering Company. After 12 years with Exxon's Corporate Research Laboratories, Ross joined Engelhard Corporation. Ross recently completed 25 years at Engelhard / BASF Corporation where he is currently a Senior Research Associate.

Ross has made pioneering contributions to the chemistry and engineering of catalytic processes. Early in his career with his advisor Michel Boudart, he developed an experimental method to address artifacts in kinetic data; a test accepted today as being definitive for kinetic control in catalysis. At Exxon, Ross' studies in Fischer-Tropsch synthesis demonstrated the crucial role intraparticle diffusion played in enhancing hydrocarbon chain length and in changing selectivity. At Engelhard, he developed important concepts in fluid catalytic cracking to help design commercial catalysts. He elucidated the mechanism by which vanadium causes structural degradation of Y zeolite in FCC catalysts, and used this understanding to minimize its deleterious effect. His studies provided a definite assessment of the role of ZSM-5 additives in FCC to form light olefins and high octane gasoline. And, he defined the critical role rare earth cations play in Y-based FCC catalysts, demonstrating how the presence of rare earth influences hydride transfer reactions and product selectivity in FCC. Most recently, at BASF, Ross, together with colleagues in academia, elucidated the mechanism of the water gas shift reaction on copper, evincing parameters that could significantly improve catalytic activity. Importantly, though, Ross has used his conceptual and mechanistic approach to catalyst research to design commercial catalysts. He is the coinventor and developer of the Reduxion – Maxol® family of FCC catalysts and of the IsoPlus® and Ultrium® families; all of which have been used commercially worldwide. He coinvented the Flex-Tec® resid cracking catalyst which has been widely and successfully deployed in demanding resid cat-cracking processes. And most recently he has developed several copper based catalysts for the petrochemical industry.

Ross chaired the 1996 Gordon Research Conference on Catalysis, and in 2009 was awarded the AIChE Catalysis and Reaction Engineering Division Practice Award.