

Low Temperature Plasma Surface Treatment of Catalytic Material

George H. Miley*, Shailendra N. Srivastava**, Kyujung Kim*, George Chen**

*NPL Associates, Inc.

912 W Armory Ave, Champaign, Illinois 61821

**Illinois Applied Research Institute

2100 S Oak St Suite 206, Champaign, Illinois 61820

ABSTRACT

Enhancing the performance of heterogeneous catalysts through plasma treatment has many applications in industry. One way to improve catalytic activity is through plasma treatment of surface “structure-sensitive” catalysts to create defects which can serve as possible catalytic reaction sites. The purpose of the plasma treatment process is to increase catalytic performance of various catalytic material.

Keywords: plasma, heterogeneous catalysts, plasma treatment / modification / irradiation

1 INTRODUCTION

In this paper we emphasize the application of the plasma treatment method to improve a variety of commercial processes that employ catalysts. However in a closely related paper at this meeting we discuss using the plasma treatment method to improve PEM fuel cell catalysts [1]. Heterogeneous catalysts are in a different phase than the reactants. Homogeneous catalysts are in the same phase as the reactants. Homogeneous catalysts have high activity and selectivity [2] compared to heterogeneous catalyst. As with most real world situations there are tradeoffs; for example heterogeneous catalyst which produce good reaction rates are sometimes composed of noble metals (e.g. platinum, palladium, etc.) which are scarce and expensive [3]. There are a variety ways to try to circumvent these tradeoffs [2] [4], but none have been fully successful to date. The process under study here uses a low temperature plasma to enhance catalytic performance of heterogeneous catalysts.

2 BACKGROUND

Heterogeneous catalyst can be classified by surface “structure-sensitive” and surface “structure-insensitive.” These classifications partially explain the catalytic reaction mechanism of the heterogeneous catalyst. The catalytic activity of structure-sensitive catalyst as the name suggest depends on the structure

of the surface. That is certain sites on the surface of the catalysts enhance the rate of the chemical reactions [4] [5] [6] [7]. Finding, predicting, and understanding the mechanism by which these certain reaction sites promote chemical reactions is still not well understood [6] [7]. This is because measuring or observing chemical reactions on the catalytic reaction site while it is taking place has never been performed. What is known are some qualitative observations such as, for structure-sensitive catalyst the reaction rate greatly increases with the number of surface defects (e.g. steps, kinks, etc.) [6] [7] [8]. This observation is based on experiments comparing reaction rates of catalyst with single-crystal surfaces and catalyst containing many surface defects [7].

In addition to surface defects other factors that enhance catalytic activity include the surface area, increasing the surface area of the heterogeneous catalyst also increase the catalytic reaction rate [9]. Furthermore catalytic reactions of materials with equal surface areas may also differ depending on their actual form [9]. For example, materials that are normally inert in macroscopic solid form (e.g. gold), demonstrate high catalytic activity in submicron solid form [10].

Low temperature plasma discharges are used in a variety of processes; for example the manufacture of semiconductor products. In the manufacturing process the plasma is used to manipulate the surface of solid materials. The effects of plasmas on surfaces are numerous, plasmas can damage the surfaces of materials through ion bombardment which can eject surface atoms a process called sputtering. Along with surface defects and damage from exposure to plasma, submicron structures have been shown to form on material surfaces under exposure to certain types of plasmas.

The effects caused by plasma-surface interaction (notably surface damage and defects, as well as the formation of submicron structures) are utilized to possibly alter the heterogeneous catalysts surface so the catalytic activity can be enhanced. The plasma-

catalysts treatment process has been studied for some time [11].

3 EXPERIMENT

Figure 1 shows a schematic of a DC plasma discharge system with the cathode (exposed to the plasma) made out of a conducting heterogeneous catalysts. Exposing the catalysts to the plasma allows the plasma to modify the catalysts surface.

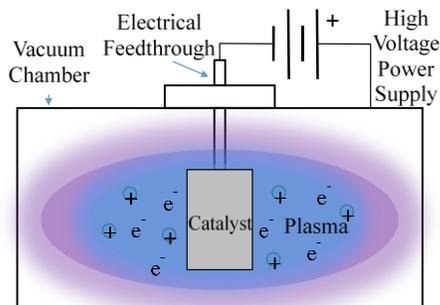


Figure 1: Schematic of DC plasma source modifying the surface of a conducting heterogeneous catalysts.

Figure 1 is a schematic of one possible system and is not the only configuration possible. A DC system is presented here because DC plasma systems are relatively simple compared to other plasma systems. However many heterogeneous catalysts are not electrically conducting. In such a case an AC discharge may be more appropriate to treat the surfaces of such catalysts. AC plasma discharges include DBD, RF, and microwave. RF, microwave are classified as AC, the distinction that separates them are the frequencies. As mentioned before using an AC discharge allows for the treatment of a greater variety of heterogeneous catalysts, however AC systems are more complicated usually requiring impedance matching which increases costs.

Heterogeneous catalytic material is being plasma-treated to modify the surface. The plasma-surface irradiation coarsens the surface of the catalytic material creating very pack submicron structures and defects [12] [13] [14] [15] [16] [17]. These submicron formations and defects on the catalytic material can serve as reactant adsorption and reaction sites [4] [5] [6] [7] [18] [19] [20]. The plasma modification can potentially increase the number reaction sites this can greatly improve the performance of the catalytic material. The plasma-surface treatment is relatively simple and can possibly enhance the catalytic activity of many less expensive heterogeneous catalysts. This then holds promise for lowering costs and/or raising

the performance of catalysts for a variety of industrially and commercially useful chemical reactions. This could allow plasma treated catalysts to supplant the more expensive catalysts currently used. Furthermore plasma irradiating some of the more expensive catalysts can also increase their catalytic activity, thereby increasing reaction rates and ultimately improving the economics without changing the catalysts employed in the process. The plasma treatment is a simple method to increase heterogeneous catalyst performance; these catalysts are ubiquitous in many industries.

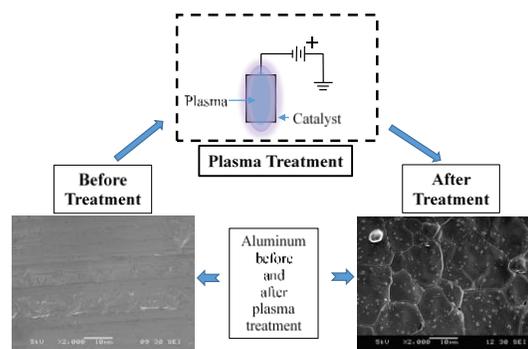


Figure 2: Plasma processing of aluminum foil demonstrating the effects of plasma on material surfaces.

Figure 2 illustrates a DC plasma treatment system currently set up to study and optimize this catalysts treatment process. As shown, initial measurements using SEM photos of surfaces before and after treatment are used to identify the nature of the surface changes. The case shown is for an aluminum foil. In addition to SEM scans, changes in the catalysts reactivity will be measured.

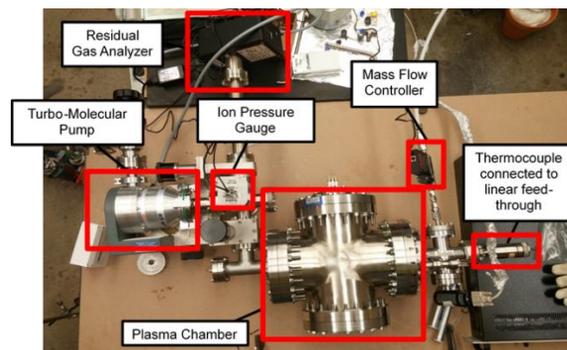


Figure 3: Experimental set up at UIUC to plasma treat various conducting materials.

Figure 3 shows a setup at the University of Illinois at Urbana-Champaign used to treat various conducting materials. The setup is a DC discharge similar to the one shown in figure 1. Various diagnostics are

connected to the chamber such as thermocouples and a RGA. The pressure in the system can be very low by using the turbo-molecular pump; this low pressure helps reduce contamination and allows better process control.

4 CONCLUSION

This plasma treatment technique can also be applied to other electrically insulating catalysts through the use of other types of plasma discharges (e.g. AC discharges). The ability to increase the performance of catalysts can also have a profound impact on numerous industries such as energy and pharmaceuticals just to name a few. Catalysts are ubiquitous in chemistry and enhancing the activity of catalyst through simple plasma treatment can ripple through the commercial sector ultimately lowering cost of products and services for the public. This approach can also allow the introduction of previous cost prohibitive technologies (e.g. fuel cell vehicles) to the market. According to FRPT Research the global market value for catalyst will be worth over \$20-billion by 2021 [21]. Even small improvements can result in large financial savings.

REFERENCES

- [1] G. H. Miley, S. N. Srivastava and G. Chen, "Catalytic Performance Enhancement by Low Temperature Plasma Treatment," in *TechConnect World 2015*, Washington, DC, 2015.
- [2] M. P. de Almeida and S. A. C. Carabineiro, "The Best of Two Worlds from the Gold Catalysis Universe Making Homogeneous Heterogeneous," *CHEMCATCHEM*, vol. 4, pp. 18-29, 2012.
- [3] M. Armbruster, K. Kovnir, M. Friedrich, D. Teschner, G. Wowsnick, M. Hahne, P. Gille, L. Szentmiklosi, M. Feuerbacher, M. Heggen, F. Girgsdies, D. Rosenthal, R. Schlogl and Y. Grin, "Al₁₃Fe₄ as a low-cost alternative for palladium in heterogeneous hydrogenation," *Nature Materials*, vol. 11, pp. 690-693, 2012.
- [4] S. He, C. Li, H. Chen, D. Su, B. Zhang, X. Cao, B. Wang, M. Wei, D. G. Evans and X. Duan, "A Surface Defect-Promoted Ni Nanocatalyst with Simultaneously Enhanced Activity and Stability," *Chemistry of Materials*, vol. 25, pp. 1040-1046, 2013.
- [5] M. Boudart, "Heterogeneous Catalysis By Metals," *Journal of Molecular Catalysis*, vol. 30, pp. 27-38, 1985.
- [6] T. Zambelli, J. Wintterlin, J. Trost and G. Ertl, "Identification of the "Active Sites" of a Surface-Catalyzed Reaction," *Science*, vol. 273, pp. 1688-1690, 1996.
- [7] Z.-P. Liu and P. Hu, "General Rules for Predicting Where a Catalytic Reaction Should Occur on Metal Surfaces: A Density Functional Theory Study of C-H and C-O Bond Breaking/Making on Flat, Stepped, And Kinked Metal Surfaces," *Journal of the American Chemical Society*, vol. 125, pp. 1958-1967, 2003.
- [8] R. T. Vang, K. Honkala, S. Dahl, E. K. Vestergaard, J. Schnadt, E. Laegsgaard, B. S. Clausen, J. K. Norskov and F. Besenbacher, "Controlling the catalytic bond-breaking selectivity of Ni surfaces by step blocking," *Nature Materials*, vol. 4, pp. 160-162, 2005.
- [9] U. Heiz, F. Vanolli, A. Sanchez and W. D. Schneider, "Size Dependent Molecular Dissociation on Mass-Selected, Supported Metal Clusters," *Journal of the American Chemical Society*, vol. 120, pp. 9668-9671, 1998.
- [10] A. Sanchez, S. Abbet, U. Heiz, W. D. Schneider, H. Hakkinen, R. N. Barnett and U. Landman, "When Gold Is Not Noble: Nanoscale Gold Catalysts," *Journal of Physical Chemistry A*, vol. 103, pp. 9573-9578, 1999.
- [11] C.-j. Liu, G. P. Vissokov and B. W.-L. Jang, "Catalyst preparation using plasma technologies," *Catalysis Today*, vol. 72, pp. 173-184, 2002.
- [12] Y. Zayachuk, A. Manhard, M. H. J. 't Hoen, W. Jacob, P. A. Zeijlmans van Emmichoven and G. van Oost, "Depth profiling of the modification induced by high-flux deuterium plasma in tungsten and tungsten-tantalum alloys," *Nuclear Fusion*, vol. 54, no. 123013, 2014.
- [13] H. Y. Xu, G. N. Luo, H. Schut, Y. Yuan, B. Q. Fu, A. Godfrey, W. Liu and G. D. Temmerman, "Enhanced modification of tungsten surface by nanostructure formation during high flux deuterium plasma exposure," *Journal of Nuclear Materials*, vol. 447, pp. 22-27, 2014.
- [14] M. Laurent-Brocq, N. Job, D. Eskenazi and J.-J. Pireaux, "Pt/C catalyst for PEM fuel cells: Control of Pt nanoparticles characteristics through a novel plasma deposition method," *Applied Catalysis B: Environmental*, vol. 147, pp. 453-463, 2014.

- [15] S. M. M. Coelho, F. D. Auret, P. J. Janse van Rensburg and J. M. Nel, "Unexpected properties of the inductively coupled plasma induced defect in germanium," *Physica B*, vol. 439, pp. 97-100, 2014.
- [16] O. V. Ogorodnikova, J. Roth and M. Mayer, "Deuterium retention in tungsten in dependence of the surface conditions," *Journal of Nuclear Materials*, Vols. 313-316, pp. 469-477, 2003.
- [17] T. Takimoto, K. Takeshita, S. Nakamura and T. Okumura, "Effects of plasma-induced defects on electrical characteristics of AlGaIn/BaN heterostructure before and after low-temperature annealing," *Thin Solid Films*, vol. 557, pp. 212-215, 2014.
- [18] R. C. Egeberg, S. Ullmann, I. Alstrup, C. B. Mullins and I. Chorkendorff, "Dissociation of CH₄ on Ni(1 1 1) and Ru(0 0 1)," *Surface Science*, vol. 497, pp. 183-193, 2002.
- [19] H. Uetsuka, K. Watanabe, H. Kimpara and K. Kunimori, "Structure Sensitivity in the Kinetics and the Dynamics of CO Oxidation over Stepped Pd(335) Studied by the Molecular Beam Infrared Chemiluminescence Technique: Determination of Working Sites during the Steady-State Reaction," *Langmuir*, vol. 15, pp. 5795-5799, 1999.
- [20] B. Hammer, "Bond Activation at Monatomic Steps: NO Dissociation at Corrugated Ru(0001)," *Physical Review Letters*, vol. 83, no. 18, pp. 3681-3684, 1999.
- [21] FRPT Research, "Global market for catalysts to be worth over \$20-bn by 2021: Report," FRPT Research, 2015.