The importance of being together
Controlling the coordination of platinum boosts catalytic reaction rates

By Ifan E. L. Stephens,1,2 Joseph S. Elias,1 and Yang Shao-Horn*1

Platinum catalyzes several chemical and electrochemical reactions that are central to humankind’s use of energy, such as the electrochemical reduction of molecular oxygen, carbon monoxide oxidation, and the water-gas shift reaction to produce carbon dioxide and hydrogen from carbon monoxide and water. Two reports in the current issue provide insights into which platinum coordination number—defined as the number of nearest neighbors—may provide the highest catalytic activities for these reactions. On page 185, Calle-Vallejo et al. use the concept of generalized coordination numbers to show that concave atomic sites on a platinum single-crystal are highly active for oxygen electroreduction (1). On page 189, Ding et al. use spectroscopic techniques to determine what role isolated Pt atoms play in CO oxidation and the water-gas shift reaction (2).

Generally speaking, the lower the coordination number, the stronger the surface interacts with reaction intermediates (3). Maximum reaction rates can be obtained when the binding of reaction intermediates to the surface is neither too strong nor too weak, yielding a “Sabatier volcano” (see the figure) named after the French chemist Paul Sabatier. Lowering the coordination number of platinum by increasing the number of steps on single-crystal platinum surfaces leads to a slight increase in the rates of electrochemical oxygen reduction (4, 5). On the other hand, increasing the number of steps on platinum surfaces can boost the rates of CO oxidation substantially (6–8). This observation has motivated the preparation of CO oxidation catalysts that minimize the coordination number of platinum through use of small clusters and isolated atoms on oxide supports (9).

Calle-Vallejo et al. now predict that concave surface sites should exhibit higher catalytic activity than a Pt(111) surface due to their reduced binding strength with reaction intermediates. Such concave sites may be obtained by placing Pt atoms in a cavity with increased coordination relative to a Pt(111) surface. The study builds on previous work reporting that the binding between a Pt(111) surface and OH, the key reaction intermediate, is slightly too strong for optimized oxygen reduction (10). Accordingly, increasing the coordination number should increase the catalytic activity. Similarly, ligand (11) and strain effects (12) from alloying with platinum also weaken the binding of OH, thus increasing catalytic activity (13).

Calle-Vallejo et al. use the concept of generalized coordination number (CN), which takes into account interactions with next-nearest neighbors as well as nearest neighbors. Because CN linearly correlates with binding energies of reaction intermediates, it can be used to describe catalytic activity (see the figure). The authors performed simple, yet elegant, electrochemical treatments to engineer such defects into a Pt(111) surface. The oxygen reduction activity of these surfaces was three times that of bulk Pt(111). Such metastable concave structures may be responsible for the high activities of nanocatalysts such as dealloyed nanoparticles, hollow nanoparticles, and Pt-Ni nanoframes (14).

Generalized coordination numbers are simple and intuitive. Moreover, in combination with prior knowledge of the relationship between binding energies and reaction rates for any given reaction (10), they clearly have predictive power. Further work is needed to provide direct evidence for the concave structures—for instance, using scanning tunneling microscopy. Moreover, the CN descriptor could be developed to incorporate the effect of water coadsorbed with OH; this would likely account for the activity of stepped Pt surfaces for oxygen reduction (4, 5).

Ding et al. explore the nature of the active sites on oxide-supported platinum catalysts that catalyze both CO oxidation and the water-gas shift reaction. Using elegant site-specific techniques that probe the entirety of the catalyst, they show that
isolated platinum atoms on oxide supports bind CO too strongly to be active. Rather, the authors find that metallic platinum sites on nanoparticles catalyze the reactions. Framing these results in terms of the coordination number, single platinum atoms correspond to the strong-binding regime at the left of the figure. The more highly coordinated sites on small nanoparticles are closer to the apex of the figure.

In contrast to previous work (9), Ding et al.’s results suggest small metallic Pt nanoparticles, rather than isolated Pt atoms, give rise to enhanced catalysis of CO. The applicability of these findings will depend on the elemental composition of the catalyst and electronic interactions between the support and the metal. For example, unlike platinum, making gold catalytically active requires atomically dispersed atoms rather than larger nanoparticles (15). Further work is needed to identify which exact sites on platinum nanoparticles (for example, terrace, edge, kink, or corner sites) are active for CO oxidation and water-gas shift catalysis. Of particular interest is the exploration of relationships between the rates of the CO oxidation/water-gas shift reactions on platinum and the generalized coordination number introduced by Calle-Vallejo and co-workers (see the figure).

The implications of reaction rate sensitivity to coordination number for heterogeneous catalysis are both subtle and far-reaching. The rational design of catalysts for heterogeneous processes requires a detailed understanding of the interplay of both the electronic structure of the catalyst surface and its local coordination environment. The insights described in (1, 2) highlight the immense opportunities for catalyst discovery and improvement provided by detailed understanding of the nature of active sites. ■

REFERENCES
1. F. Calle-Vallejo et al., Science 350, 185 (2015).
2. K. Ding et al., Science 350, 189 (2015).
3. T. Jiang et al., J. Phys. Chem. C 113, 10548 (2009).
4. A. Kuzum, E. Herrero, J. M. Feliu, J. Electroanal. Chem. 599, 333 (2007).
5. A. S. Bandarenka, H. A. Hansen, J. Rossmeissl, I. E. L. Stephens, Phys. Chem. Chem. Phys. 16, 13625 (2014).
6. S. W. Lee et al., J. Phys. Chem. C 131, 15669 (2009).
7. S. C. S. Lai, N. P. Lebedeva, T. M. H. Housmans, M. T. M. Koper, Top. Catal. 46, 320 (2007).
8. J. Z. Xu, J. T. Yates, J. Chem. Phys. 99, 725 (1993).
9. Q. Fu, H. Saib, M. Fytianu-Stephanopoulos, Science 301, 935 (2003).
10. J. K. Narskov et al., J. Phys. Chem. B 108, 17886 (2004).
11. J. R. Kitchin, J. K. Narskov, M. A. Barteau, J. G. Chen, Phys. Rev. Lett. 93, 156801 (2004).
12. M. Mavrikakis, B. Hammer, J. K. Narskov, Phys. Rev. Lett. 81, 2819 (1998).
13. V. R. Stamenkovic et al., Science 315, 493 (2007).
14. P. Strasser, Science 349, 379 (2015).
15. M. Yang et al., Science 346, 1498 (2014).

FOOD SCIENCE

Designing a sustainable diet
Sustainability as dietary guidance created political debate

By Kathleen Merrigan,* Timothy Griffin, Parke Wilde, Kimberly Robien, Jeanne Goldberg,* William Dietz*

In the United States, a vigorous debate is under way over government-issued dietary guidance. A February 2015 report by the U.S. Dietary Guidelines Advisory Committee (DGAC) recommended, for the first time, that food system sustainability be an integral part of dietary guidance in the 2015 Dietary Guidelines for Americans (DGAs) (1). With the final decision from the secretaries of Health and Human Services (HHS) and of Agriculture (USDA) about what parts of the DGAC recommendations to include in the 2015 DGAs expected at the end of this year, we discuss the need to incorporate sustainability into dietary guidelines and the political maneuvering under way to excite it. DGAs, which are updated every 5 years, have consistently recommended a diet higher in plant-based foods and lower in animal-based foods. This year DGAC concluded that “consistent evidence” suggests that such a dietary pattern is not only more healthful but also is associated with less environmental impact than the average American diet (1). This rationale has ignited controversy (2).

Dietary guidelines are not unique to the United States. The United Nations Food and Agriculture Organization (FAO) posts dietary guidelines by 67 national governments. The purpose of such guidance historically has been to educate people on how to avoid malnutrition. In the United States, DGAs are important information for nutrition professionals. Skeptics argue that DGAs are largely inconsequential. Adherence is problematic; only 4% of Americans meet DGAs, and fewer than 40% of American adults meet the healthy weight recommendation (1, 3).

Nevertheless, DGAs have tangible influence on federal programs. DGAs inform meal content for example, for (i) military personnel; (ii) 8.6 million needy Americans served by the Women, Infants, and Children program; and (iii) 31 million children served through the National School Lunch Program. DGAC recommended that the government do a better job aligning fed-

1Trachtenberg School of Public Policy and Public Administration, the George Washington University, Washington, DC 20052, USA.
2Friedman School of Nutrition Science and Policy, Tufts University, Medford, MA 02155, USA.
3Milk Institute School of Public Health, the George Washington University, Washington, DC 20052, USA.
*Corresponding author. E-mail: kmerrigan@gwu.edu