Polyoxometalates

DOI: 10.1002/anie.200805382

Are Particulate Noble-Metal Catalysts Metals, Metal Oxides, or Something In-Between?

*James C. Goloboy and Walter G. Klemperer**

cluster compounds · heterogeneous catalysis · palladium · polyoxometalates · surface chemistry

Catalysts are employed in the vast majority of industrial chemical processes, and the vast majority of these processes are heterogeneous, as they utilize solid catalysts.[1] Noble metal catalysts are of particular commercial importance, and among these catalysts, palladium- and platinum-containing materials have received particular attention in recent years owing to their role as oxidation catalysts in automobile emission-control systems and reforming catalysts for the production of high-octane gasoline. Although these noble metal catalysts have been the object of intensive study for almost two hundred years, their precise structure and composition is ill-defined on the sub-nanometer scale, as they are generally employed as finely divided particulates with dimensions of about 10–20 Å. A host of well-defined metal cluster compounds have been prepared and studied in recent years, but they have proved to be surprisingly poor models for noble metal particulate catalysts in terms of chemical reactivity. A possible explanation for this state of affairs is the requirement that these metal particulates contain not only metal atoms, but also oxygen atoms, to achieve optimal catalytic activity. This requirement was first proposed by Döbereiner early in the nineteenth century; however it has been difficult to develop through synthesis and reactivity studies, as well-defined noble metal oxide clusters were unknown. The situation has now changed: Kortz and co-workers recently reported the palladium heteropolyanion $[Pd^{II}_{13}As^{V}_{8}O_{34}(OH)_6]^{8-}$.[2] The $\{Pd_{13}O_{32}\}$ core structure of this species is of seminal importance, as it is potentially the forerunner of a family of reactive noble metal oxide cluster compounds capable of providing insights into the detailed molecular mechanism of catalysis by noble metal particulates.

But first some history: Noble metal catalysis was first reported in 1817, when Humphrey Davy observed that hot palladium and platinum metal surfaces would support flameless combustion of several different inorganic and organic vapors.[3] Shortly thereafter, two new forms of noble metal catalysts were prepared that serve as catalysts at ambient temperature or below: Edmund Davy prepared the first noble metal "black" by solution chemical reduction of platinum salts,[4] and Döbereiner prepared the first noble metal "sponge" by pyrolysis of ammonium hexachloroplatinate.[5] Liebig then examined both platinum black and platinum sponge and found them to be nothing more than finely divided platinum metal,[6] but Döbereiner begged to differ, pointing out that finely divided platinum metal, unlike platinum black or sponge, absorbs large amounts of oxygen.[7] Döbereiner's view that particulate platinum catalysts were not simply finely divided metals but rather finely divided metals plus adsorbed oxygen might be regarded as a semantic argument, as any catalytic cycle allows for more than one intermediate species to be defined as a catalyst. Either metal or metal plus oxygen might thus be equally well called the catalyst in a catalytic oxidation process. However, studies of noble metal hydrogenation catalysts in the early twentieth century revealed that platinum and palladium black (and colloidal) catalysts were activated by oxygen;[8,9] Langmuir even demonstrated that clean bulk platinum metal surfaces could be rendered catalytically active for the room temperature reaction of hydrogen with oxygen by first bringing the surfaces in contact with hydrogen and oxygen at elevated temperature.[10] According to Somorjai and co-workers, adsorbed oxygen influences not only the activity of platinum-catalyzed hydrocarbon hydrogenation and dehydrogenation, but also the selectivity.[11]

In recent years, surface scientists have determined the structure and stoichiometry of several oxide phases formed on single-crystal noble metal surfaces, which are important models for heterogeneous catalysts. For example, Rh_8O_{18} chains are formed on oxidized Rh(110) (Figure 1 a–c),[12] and these same chains have been observed on Rh(331) in a different structural environment.[13] Controlled oxidation of Pt(110) yields analogous $Pt_{10}O_{22}$ chains,[14] and formation of "infinite" planar $\{PtO_2\}_n$ chains has been proposed on Pt(332) surfaces.[15] Note that this type of chain is observed not only on noble metal surfaces, but also in oxometalate salts: Na_2PtO_2[16] contains $\{Pt^{II}O_2^{2-}\}_n$ chains; Li_2PdO_2,[17] K_2PdO_2,[18] and Ag_2PdO_2[19] contain $\{Pd^{II}O_2^{2-}\}_n$ chains; and $CaBa_2Pd_3O_6$[20] contains the cyclic polyoxometalate analogue $\{Pd^{II}O_2^{2-}\}_6$ (Figure 1 d).

Given the structural analogy between noble metal single-crystal surface oxides and crystalline oxometalate salts, it is tempting to inquire whether a similar analogy might exist between high-nuclearity noble metal clusters and polyoxometalate clusters. The polyoxometalate cluster reported by Kortz and co-workers[2] allows this question to be addressed

---

[*] J. C. Goloboy, Prof. W. G. Klemperer
Department of Chemistry, University of Illinois at Urbana-Champaign
Urbana, IL 61801 (USA)
E-mail: wklemper@uiuc.edu

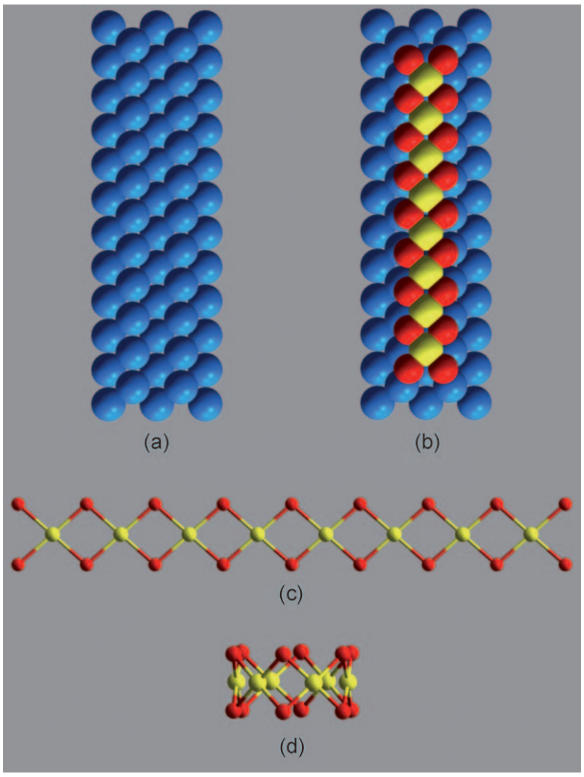

Figure 1. a) Space-filling model of an unreconstructed fcc metal (110) surface. b) Space-filling model showing the structural environment of Rh_8O_{18} on the Rh(110)-(10×2)-O surface.[12] c) Ball-and-stick model of the Rh_8O_{18} chain observed on the Rh(110)-(10×2)-O surface. d) Ball-and-stick model of the $[Pd^{II}_6O_{12}]^{12-}$ ring in $CaBa_2Pd_3O_6$.[20] Metal atoms: blue/yellow, O red.

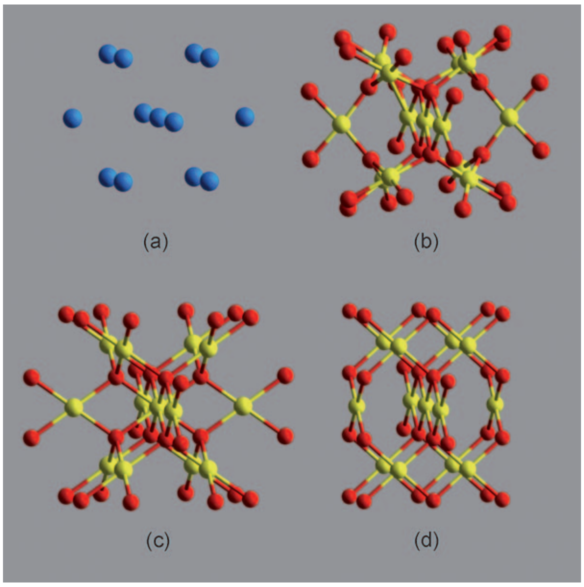

Figure 2. a) Centered cuboctahedral $\{Pd_{13}\}$ fragment of $[Pd_{30}(CO)_{26}(PEt_3)_{10}]$ and $[Pd_{54}(CO)_{40}(PEt_3)_{14}]$.[21] b) The $[Pd^{II}_{13}O_{32}]^{38-}$ core structure of $[Pd^{II}_{13}As^{V}_{8}O_{34}(OH)_6]^{8-}$.[2] c) Idealized $[Pd^{II}_{13}O_{32}]^{38-}$ structure. d) $\{Pd^{II}_{13}O_{28}\}^{30-}$ fragment of the PdO structure. Pd^0 blue, Pd^{II} yellow, O red.

for the first time by providing the metal oxide counterpart to previously reported noble metal clusters. If the analogy exists, noble metal clusters and metal oxide clusters define the extremes between which particulate noble metal catalysts lie, potentially offering insight into the nature of (partially oxidized) particulate metal catalysts. The cubic-closest-packed $\{Pd_{13}\}$ metal cluster structure (Figure 2a) is a persistent motif in high-nuclearity palladium clusters such as $[Pd^0_{30}(CO)_{26}(PEt_3)_{10}]$ and $[Pd^0_{54}(CO)_{40}(PEt_3)_{14}]$.[21] As shown in Figure 2b, the metal centers in the $\{Pd^{II}_{13}O_{32}\}^{38-}$ core of $[Pd^{II}_{13}As^{V}_{8}O_{34}(OH)_6]^{8-}$[2] closely approximate the centered cuboctahedral geometry shown in Figure 2a. This same structure can be idealized (Figure 2c), where the metal centers adopt a rigorous cubic-closest-packed structure and the oxygen atoms occupy positions defined by the tetrahedral interstices in an extended cubic-closest-packed array of metal atoms. This structure is reminiscent of the $Pd^{II}O$ structure, which is obtained by first filling half of the tetrahedral interstices in a cubic-closest-packed palladium atom array, and then distorting the structure such that palladium(II) coordination geometry is approximately square. Note that palladium coordination is cubic for the central palladium atom and rectangular for the peripheral palladium atoms in the idealized $[Pd^{II}_{13}O_{32}]^{38-}$ structure shown in Figure 2c. Its actual structure is also distorted in such a way that the palladium(II) coordination geometry (Figure 2b) approximates a square. By comparing Figures 2b and 2d, it is evident that the observed $\{Pd_{13}O_{32}\}$ structure is not a fragment of the $Pd^{II}O$ structure. To summarize: Just as the Pd_{13} cluster shown is a fragment of the cubic-closest-packed structure adopted by palladium metal, the $\{Pd_{13}O_{32}\}$ cluster is a fragment of a structure composed of closest-packed palladium atoms plus interstitial oxygen atoms.

How then does the $[Pd^{II}_{13}As^{V}_{8}O_{34}(OH)_6]^{8-}$ heteropolyanion relate to the problem of defining the structure and stoichiometry of platinum metal particulate catalysts? As Döbereiner first pointed out, these particulates are neither metals nor metal oxides, but something in-between; he initially referred to platinum black as a "suboxide".[22] As known low-valent noble metal cluster compounds and the divalent noble metal polyoxometalate of Kortz et al. define the extremes in terms of oxygen content, it is now possible to imagine "something in-between" as a molecular mixed-valent metal cluster in which oxygen atoms occupy some but not all of the interstitial sites. Bulk palladium metal is known to form an interstitial suboxide PdO_x,[23] so formation of a "suboxide cluster" is a real possibility, and one that will undoubtedly command the attention of synthetic inorganic chemists for some time to come.

---

[1] *Handbook of Heterogeneous Catalysis*, *Vol. 1*, 2nd ed. (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. v–vi.

[2] E. V. Chubarova, M. H. Dickman, B. Keita, L. Nadjo, F. Miserque, M. Mifsud, I. W. C. E. Arends, U. Kortz, *Angew. Chem.* **2008**, *120*, 9685–9689; *Angew. Chem. Int. Ed.* **2008**, *47*, 9542–9546.

[3] H. Davy, *Philos. Trans. R. Soc. London* **1817**, *107*, 77 – 85.
[4] E. Davy, *Philos. Trans. R. Soc. London* **1820**, *110*, 108 – 125.
[5] J. W. Döbereiner, *J. Chem. Phys.* **1823**, *38*, 321 – 326.
[6] J. Liebig, *Ann. Phys.* **1829**, *93*, 101 – 114.
[7] J. W. Döbereiner, *Zur Chemie des Platins in wissenschaftlicher und technischer Beziehung*, P. Balz'sche Buchhandlung, Stuttgart, **1836**, p. 6 and 69.
[8] R. Willstätter, E. Waldschmidt-Leitz, *Ber. Dtsch. Chem.* **1921**, *54*, 113 – 138.
[9] R. Adams, R. L. Shriner, *J. Am. Chem. Soc.* **1923**, *45*, 2171 – 2179.
[10] I. Langmuir, *J. Am. Chem. Soc.* **1918**, *40*, 1361 – 1403.
[11] C. E. Smith, J. P. Biberian, G. A. Somorjai, *J. Catal.* **1979**, *57*, 426 – 443.
[12] E. Vesselli, C. Africh, A. Baraldi, C. Comelli, F. Esch, R. Rosei, *J. Chem. Phys.* **2001**, *114*, 4221 – 4225.
[13] J. Gustafson, A. Resta, A. Mikkelsen, R. Westerström, J. N. Andersen, E. Lundgren, J. Weissenrieder, M. Schmid, P. Varga, N. Kasper, X. Torrelles, S. Ferrer, F. Mittendorfer, G. Kresse, *Phys. Rev. B* **2006**, *74*, 035401.
[14] W. X. Li, L. Österlund, E. K. Vestergaard, R. T. Vang, J. Matthiesen, T. M. Pedersen, E. Lægsgaard, B. Hammer, F. Besenbacher, *Phys. Rev. Lett.* **2004**, *93*, 146104.
[15] J. G. Wang, W. X. Li, M. Borg, J. Gustafson, A. Mikkelsen, T. M. Pederesen, E. Lundgren, J. Weissenrieder, J. Klikovits, M. Schmid, B. Hammer, J. N. Andersen, *Phys. Rev. Lett.* **2005**, *95*, 256102.
[16] W. Urland, R. Hoppe, *Z. Anorg. Allg. Chem.* **1972**, *392*, 23 – 36.
[17] R. Wolf, R. Hoppe, *Z. Anorg. Allg. Chem.* **1986**, *536*, 77 – 80.
[18] H. Sabrowsky, W. Bronger, D. Schmitz, *Z. Naturforsch. B* **1974**, *29*, 10 – 12.
[19] M. Schreyer, M. Jansen, *Solid State Sci.* **2001**, *3*, 25 – 30.
[20] P. Sonne, H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1004 – 1006.
[21] E. G. Mednikov, S. A. Ivanov, L. F. Dahl, *Angew. Chem.* **2003**, *115*, 337 – 341; *Angew. Chem. Int. Ed.* **2003**, *42*, 323 – 327.
[22] J. W. Döbereiner, *Ann. Phys.* **1822**, *72*, 193 – 206.
[23] A. G. Christy, S. M. Clark, *Phys. Rev. B* **1995**, *52*, 9259 – 9265.