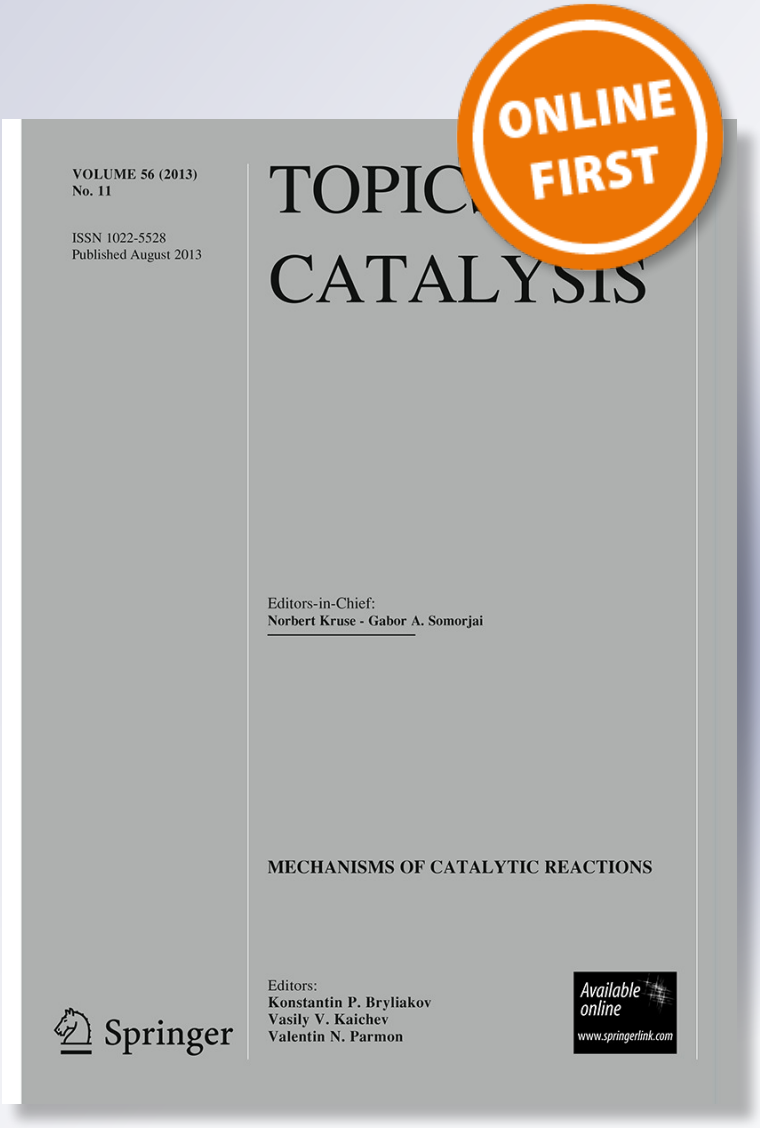
D. W. ("Wayne") Goodman: A Pioneer in Elucidating the Relationships Between Surface Structure of Catalysts and Their Performance, and in Using Model Catalysts for That Purpose

Charles T. Campbell

Topics in Catalysis

ISSN 1022-5528

Top Catal
DOI 10.1007/s11244-013-0136-9



Springer

Top Catal
DOI 10.1007/s11244-013-0136-9

ORIGINAL PAPER

D. W. ("Wayne") Goodman: A Pioneer in Elucidating the Relationships Between Surface Structure of Catalysts and Their Performance, and in Using Model Catalysts for That Purpose

Charles T. Campbell

Professor D. Wayne Goodman in his lab at Texas A&M University some time before his death

This special issue on "Structure/Function Relationships in Heterogeneous Catalysis: Insights using Well-Defined Model Catalysts" is dedicated to the memory of Professor D. Wayne Goodman for his many seminal contributions to our understanding of heterogeneous catalysis. His creative experiments using well-defined model catalysts decisively identified many surface structure–function relationships for bimetallic catalysts and oxide-supported metal nanoparticle catalysts and their underlying mechanistic explanations. Goodman is internationally recognized for his highly impactful contributions which truly paved the way for many of the other groups who later became active in this arena. His papers and talks in this area eloquently outlined how one could approach industrially-important fundamental questions in catalysis. Many researchers picked up on the excitement and clear-headed logic he projected in his talks, subsequently shifting their own research to use the new approaches he had established. As much as any other researcher, Prof. Goodman set the direction for the field of surface chemistry research related to heterogeneous catalysis from 1980 until 2010.

Goodman's research had a clear central theme: the use of surface science techniques to understand the chemistry associated with solid surfaces. He also pioneered many methods for measuring and correlating catalytic activity and selectivity and the structural properties of surfaces, the roles of promoters and poisons in catalytic reactions, and the nature of metal–metal bonding in mixed-metal catalysts. In this regard, he has been a major contributor to the emergence of the currently recognized field of modern surface chemistry.

Goodman received his Ph.D. in Physical Chemistry in 1975 at the University of Texas, Austin, under the supervision of M.J.S. Dewar, where his research included some of the earliest measurements and full analysis of the photoelectron spectra of inorganic molecules. After completing his Ph.D., he won a NATO fellowship, and then became an NRC Research Fellow at the National Bureau of Standards near Washington, DC. At the "Bureau" (now NIST), he worked under the supervision of two pioneers in the field of surface science, Ted Madey and John Yates. His independent scientific career took off in the early 1980s; when he became a staff member at Sandia National Laboratories in Albuquerque, NM.

One of his earliest papers in catalysis was a benchmark study where he and his coworkers at the Bureau established a direct connection between the reaction kinetics of the methanation reaction on single crystal surfaces and analogous measurements on supported metal catalysts [1]. These measurements were facilitated by the coupling of an

C. T. Campbell (✉)
Department of Chemistry, University of Washington, Seattle, WA 98195-1700, USA
e-mail: campbell@chem.washington.edu

Published online: 26 July 2013

apparatus for the measurement of reaction kinetics at elevated pressures with an ultrahigh vacuum system for surface analysis. This work is recognized as a key set of experiments that "bridged the gap" between surface science and catalysis, and clearly showed that the "structure insensitivity" of this reaction extended from complex supported catalysts to monolithic single crystals. These experiments included measurements which identified spectroscopically "active" or "carbidic" surface carbon as the primary intermediate in the methanation of carbon monoxide and "graphitic" carbon is a source of poisoning for this reaction [2, 3]. This combined work is a citation classic and frequently appears in textbooks on catalysis and surface science.

Goodman was a pioneer in the use of surface science techniques and model catalysts to study poisoning and promotion at surfaces. In particular, the effects of sulfur on a single crystal nickel catalyst for the methanation reaction were studied for the first time as a function of surface coverage [4]. These studies showed that the effects of sulfur were significantly more extensive than merely blocking sites at the surface, that is, that the effects were "long-range" in nature. This work was extended to carbon, chlorine, and phosphorus which showed that the extent of the poisoning by electronegative impurities on the chemisorptive and catalytic properties was related directly to the relative electronegativity of the surface impurity [5, 6]. This was the first systematic study of a series of electronegative impurities and their effect on surface chemistry. Subsequent work was directed toward the effects of electropositive impurities such as potassium on carbon monoxide chemisorption and reaction [7]. These combined works addressing the poisoning and promotion of surface reactions are quite unique and extensively cited in textbooks and reviews covering impurity effects on surfaces and in catalysis.

Early work by Goodman also included several important comparative studies of the oxidation of CO over single crystal catalysts and supported metal catalysts [8–12]. These studies showed an excellent continuity for this reaction over single crystal surfaces of Ru, Pd, Pt, Ir, and Rh, between the 10^{-6} and 100 Torr pressure regimes and with supported metal catalysts. His early work also included the studies of the reactive sticking of small alkanes on single crystalline metal surfaces. These so-called "bulb" experiments at elevated pressures were the first of their kind to be used in conjunction with molecular beam results to test directly the dynamical theories of the dissociative adsorption of molecules at surfaces [13, 14]. The results showed that the "direct" channel for the sticking of methane was the primary mechanism for its reactive sticking in catalytic processes at elevated pressures; however, for ethane and higher alkanes, the "precursor" route was shown to dominate.

He next set out to relate activity and selectivity in the hydrogenolysis or "cracking" of small alkanes with the surface structure of single crystal metal surfaces [15–17]. These results showed that this class of reactions is markedly "structure sensitive" and indicated the nature of the "active" sites for the reaction. The activity and selectivity for the "rough" or more open surfaces was shown to correlate well with analogous results for relatively small particles on supported catalysts. The results for the "smooth" surfaces, on the other hand, correlated well with the analogous results for the relatively large supported particles. Altogether these studies showed definitively that specific surface structure and sites define catalytic activity and selectivity for this category of reactions.

In 1988, Goodman took a faculty position in the Department of Chemistry at Texas A&M University, where he remained until his death in early 2012, holding the Robert A. Welch Foundation Chair.

At about the time he moved from Sandia to Texas A&M, Goodman began to address the mechanisms by which bimetallic catalysts demonstrate improved catalytic properties over single-component metal catalysts [18–20]. These studies showed that monolayer metal films supported on a second metal generally are electronically perturbed, and that this perturbation can dramatically alter the chemical and catalytic properties of the overlayer metal. In many cases, the metal overlayer exhibits chemisorptive and reactivity properties that are significantly different from those exhibited by the pure metal. Furthermore, a correlation was found between the surface core-level binding energies measured by X-ray photoelectron spectroscopy (XPS) and the modified peak desorption temperatures observed for CO from the metal adlayers by temperature programmed desorption (TPD). These observed trends led to a clearer understanding of the nature of the metal–metal bonding in mixed-metal catalysts. In the subsequent 20 years, he continued to make many seminal contributions to our understanding of bimetallic catalysts. A very recent example is his work in the area on PdAu alloy catalysts for vinyl acetate synthesis, where he elegantly established the atomic-level structure of the catalytically active site [21].

Goodman next turned to investigating structure/function relationships in supported metal catalysts with respect to particle size and support effects. He was the first to show how one could make great progress in this respect using well-characterized model catalysts prepared by vapor-deposited metals on ultra-thin oxide surfaces [22–34]. In doing this, his pioneering use of oxide films on refractory supports to facilitate the use of high resolution electron energy loss (HREELS) and infrared reflection absorption (IRAS) surface spectroscopies was very important in facilitating later studies of all aspects of oxide surface chemistry by many groups worldwide. The surface charging and related properties of bulk dielectric materials had precluded the routine use of these techniques previously. Goodman's

group also pioneered the use of scanning tunneling and atomic force microscopies (STM and AFM) to study the detailed microscopic morphology of model oxide and oxide-supported metal nanoparticle catalysts [33, 35–37].

One of Goodman's most important contributions has been in clarifying the relationship between structure and catalytic activity in catalysis by gold [38–47]. I know of no other paper in surface science research related to catalysis that has inspired so many other researchers into new studies as did his paper published in Science [38], where he elegantly addressed why gold catalyst particles 2–3 nm in size are exceedingly active for low-temperature CO oxidation, whereas particles larger than 6 nm are completely dead.

These research accomplishments have been recognized in a number of ways. He has received four awards from the American Chemical Society: the Ipatieff Prize in 1984; the Colloid and Surface Chemistry (Kendall) Award in 1993; the A. W. Adamson Award in 2002; and the Gabor A. Somorjai Award in 2005. In 1994 he received the Yarwood Medal of the British Vacuum Council, and a Senior Humboldt Research Award. In 2001, he received the Giuseppe Parravano Award, and in 1997 the Texas A&M Distinguished Achievement Award in Research. He has been a Distinguished Lecturer at the University of Texas, a Frontier Lecturer at Texas A&M University, the Procter and Gamble Lecturer at the University of Cincinnati, and the Langmuir Lecturer for the American Chemical Society. He was the Ipatieff Lecturer at Northwestern University in 1992, and in 1998 was appointed the Burwell Lecturer of the North American Catalysis Society. In 1984 he was listed as one of 100 Outstanding Young Scientists in America by Science Digest and in 1991, he received an Honorary Doctor of Science degree from his alma mater.

Goodman was also exemplary in his service to the community. He served as Chairman of the American Chemical Society Division of Colloid and Surface Chemistry in 1985, Vice-Chairman in 1984, and as Treasurer in 1979–1983. He was chairman of this division's continuing symposium on the Surface Science of Catalysis, and chaired numerous of its symposia at national ACS meetings. In 1988, Prof. Goodman served as chair of the Materials Research Society Fall Meeting, and, in 1992, was chair of the Gordon Conference on Catalysis. He was very active in the promotion and organization of science, and served on review and advisory committees for Oak Ridge, Pacific Northwest, Livermore, Lawrence Berkeley, and Brookhaven National Laboratories and was the international advisor to the Science and Engineering Council of Great Britain for their Catalysis Initiative. He chaired the Advisory Council for the Chemistry Division of DOE Basic Energy Sciences, and currently serves on the DOE Basic Energy Sciences Advisory Council (BESAC). He served as Associate Editor for the Journal of Catalysis, and on the advisory boards of Chemical Physics Letters, Journal of Physics-Condensed Matter, Langmuir, Applied Surface Science, Catalysis Letters and Topics in Catalysis.

On a personal level, Goodman was an exceptionally likeable, fun and supportive colleague, a steadfast friend, and a beloved husband and father. He possessed an infectious enthusiasm for science, life and people. He was a dedicated and beloved mentor to his students and postdocs, and extremely supportive of young coworkers and senior colleagues alike. He possessed incredible skills with instrumentation, and was an amazing reader, with a superb memory for and grasp of the literature, both scientific and other. He enjoyed and thrived on competition and debate. He was an inspirational and eloquent speaker. He had unsurpassed humor and story-telling ability that captured eloquently the human condition. Indeed, he was famous for his humor in his public lectures on scientific topics, which always began with one or more humorous stories widely anticipated by the audience. As a younger man he was an outstanding athlete. He was an avid pilot of experimental airplanes, and crashed from the sky three times. He prided himself on his successful attempts to defy gravity in this way, and even jokingly referred to his confidence that he could beat cancer as just another metaphorical example of doing just that. Indeed, he bought himself another plane just 2 months before his death in hopes to prove that point.

The list of authors in this issue attests to the deep respect held for Professor Goodman by the scientific community worldwide. It was an honor for me to be able to assemble their collective contributions honoring my dear friend in this issue. It is also notable that the collection of topics covered by their outstanding research papers collected here almost perfectly reflects the set of topics that were the main foci of Goodman's research. I am sure that Wayne would have been very pleased with these contributions.

References

1. Goodman DW, Kelley RD, Madey TE, Yates JT (1980) Kinetics of the hydrogenation of CO over a single-crystal nickel-catalyst. J Catal 63:226–234
2. Goodman DW, White JM (1979) Measurement of active-carbon on ruthenium(110)—relevance to catalytic methanation. Surf Sci 90:201–203
3. Goodman DW, Kelley RD, Madey TE, White JM (1980) Measurement of carbide buildup and removal kinetics on Ni(100). J Catal 64:479–481
4. Goodman DW, Kiskinova M (1981) Chemisorption and reactivity studies of H_2 and CO on sulfided Ni(100). Surf Sci 105:L265–L270
5. Kiskinova M, Goodman DW (1981) Modification of chemisorption properties by electronegative adatoms—H_2 and CO on chlorided, sulfided, and phosphided Ni(100). Surf Sci 108:64–76
6. Kiskinova M, Goodman DW (1981) Interaction of H_2 and CO with carbided and nitrided Ni(100). Surf Sci 109:L555–L559

7. Campbell CT, Goodman DW (1982) A surface science investigation of the role of potassium additives in nickel catalysts for CO hydrogenation. Surf Sci 123:413–426
8. Berlowitz PJ, Peden CHF, Goodman DW (1988) Kinetics of CO oxidation on single-crystal Pd, Pt and Ir. J Phys Chem 92: 5213–5221
9. Goodman DW, Peden CHF (1986) CO oxidation over Rh and Ru—a comparative-study. J Phys Chem 90:4839–4843
10. Oh SH, Fisher GB, Carpenter JE, Goodman DW (1986) Comparative kinetic-studies of CO–O_2 and CO–NO reactions over single-crystal and supported rhodium catalysts. J Catal 100: 360–376
11. Peden CHF, Goodman DW (1986) Kinetics of CO oxidation over Ru(0001). J Phys Chem 90:1360–1365
12. Peden CHF, Goodman DW, Blair DS, Berlowitz PJ, Fisher GB, Oh SH (1988) Kinetics of CO oxidation by O_2 or NO on Rh(111) and Rh(100) single-crystals. J Phys Chem 92:1563–1567
13. Beebe TP, Goodman DW, Kay BD, Yates JT (1987) Kinetics of the activated dissociative adsorption of methane on the low index planes of nickel single-crystal surfaces. J Chem Phys 87:2305–2315
14. Sault AG, Goodman DW (1988) Dissociative adsorption of alkanes on Ni(100)—comparison with molecular-beam results. J Chem Phys 88:7232–7239
15. Engstrom JR, Goodman DW, Weinberg WH (1986) Hydrogenolysis of n-butane over the (111) and (110)-(1×2) surfaces of iridium— a direct correlation between catalytic selectivity and surface-structure. J Am Chem Soc 108:4653–4655
16. Greenlief CM, Berlowitz PJ, Goodman DW, White JM (1987) CO methanation and ethane hydrogenolysis over Ni thin-films supported on w(110) and w(100). J Phys Chem 91:6669–6673
17. Peden CHF, Goodman DW (1987) Kinetics of cyclohexane dehydrogenation and hydrogenolysis over Ru(0001) and Cu/Ru(0001). J Catal 104:347–358
18. Rodriguez JA, Goodman DW (1991) Surface science studies of the electronic and chemical-properties of bimetallic systems. J Phys Chem 95:4196–4206
19. Rodriguez JA, Campbell RA, Goodman DW (1991) Electron-donor electron-acceptor interactions in bimetallic surfaces–theory and XPS studies. J Phys Chem 95:5716–5719
20. Rodriguez JA, Goodman DW (1992) The nature of the metal metal bond in bimetallic surfaces. Science 257:897–903
21. Chen MS, Kumar D, Yi CW, Goodman DW (2005) The promotional effect of gold in catalysis by palladium-gold. Science 310:291–293
22. Wu MC, Corneille JS, Estrada CA, He JW, Goodman DW (1991) Synthesis and characterization of ultra-thin MgO films on Mo(100). Chem Phys Lett 182:472–478
23. He JW, Estrada CA, Corneille JS, Wu MC, Goodman DW (1992) CO adsorption on ultrathin MgO films grown on a MO(100) surface—an iras study. Surf Sci 261:164–170
24. Wu MC, Truong CM, Goodman DW (1992) Electron-energy-loss-spectroscopy studies of thermally generated defects in pure and lithium-doped MgO(100) films on Mo(100). Phys Rev B 46:12688–12694
25. Wu MC, Corneille JS, He JW, Estrada CA, Goodman DW (1992) Preparation, characterization, and chemical-properties of ultrathin MgO films on MO(100). J Vac Sci Technol A 10:1467–1471
26. Xu XP, Goodman DW (1992) New approach to the preparation of ultrathin silicon dioxide films at low-temperatures. Appl Phys Lett 61:774–776
27. Xu XP, Vesecky SM, Goodman DW (1992) Infrared reflection-absorption spectroscopy and STM studies of model silica-supported copper-catalysts. Science 258:788–790
28. Xu XP, Goodman DW (1993) An infrared and kinetic-study of CO oxidation on model silica-supported palladium catalysts from 10^{-9} to 15-torr. J Phys Chem 97:7711–7718
29. Chen PJ, Goodman DW (1994) Epitaxial-growth of ultrathin Al_2O_3 films on Ta(110). Surf Sci 312:L767–L773
30. Xu XP, Chen PJ, Goodman DW (1994) A comparative-study of the coadsorption of CO and NO on Pd(100), Pd(111), and silica-supported palladium particles with infrared reflection-absorption spectroscopy. J Phys Chem 98:9242–9246
31. Rainer DR, Vesecky SM, Koranne M, Oh WS, Goodman DW (1997) The CO + NO reaction over Pd: a combined study using single-crystal, planar-model-supported, and high-surface-area Pd/Al_2O_3 catalysts. J Catal 167:234–241
32. Street SC, Xu C, Goodman DW (1997) The physical and chemical properties of ultrathin oxide films. Annu Rev Phys Chem 48:43–68
33. Rainer DR, Goodman DW (1998) Metal clusters on ultrathin oxide films: model catalysts for surface science studies. J Mol Catal A 131:259–283
34. Chusuei CC, Lai X, Luo K, Goodman DW (2001) Modeling heterogeneous catalysts: metal clusters on planar oxide supports. Top Catal 14:71–83
35. Goodman DW (1995) Model studies in catalysis using surface science probes. Chem Rev 95:523–536
36. Xu C, Lai X, Zajac GW, Goodman DW (1997) Scanning tunneling microscopy studies of the TiO_2(110) surface: structure and the nucleation growth of Pd. Phys Rev B 56:13464–13482
37. Lai X, St Clair TP, Valden M, Goodman DW (1998) Scanning tunneling microscopy studies of metal clusters supported on TiO_2 (110): morphology and electronic structure. Prog Surf Sci 59:25–52
38. Valden M, Lai X, Goodman DW (1998) Onset of catalytic activity of gold clusters on titania with the appearance of non-metallic properties. Science 281:1647–1650
39. Valden M, Pak S, Lai X, Goodman DW (1998) Structure sensitivity of CO oxidation over model Au/TiO_2 catalysts. Catal Lett 56:7–10
40. Lai XF, Goodman DW (2000) Structure-reactivity correlations for oxide-supported metal catalysts: new perspectives from STM. J Mol Catal A 162:33–50
41. Choudhary TV, Goodman DW (2002) Oxidation catalysis by supported gold nano-clusters. Top Catal 21:25–34
42. Goodman DW (2003) Model catalysts: from imagining to imaging a working surface. J Catal 216:213–222
43. Chen MS, Goodman DW (2004) The structure of catalytically active gold on titania. Science 306:252–255
44. Meier DC, Goodman DW (2004) The influence of metal cluster size on adsorption energies: CO adsorbed on Au clusters supported on TiO_2. J Am Chem Soc 126:1892–1899
45. Chen MS, Goodman DW (2006) Catalytically active gold: From nanoparticles to ultrathin films. Acc Chem Res 39:739–746
46. Chen MS, Goodman DW (2006) Structure-activity relationships in supported Au catalysts. Catal Today 111:22–33
47. Chen MS, Goodman DW (2008) Catalytically active gold on ordered titania supports. Chem Soc Rev 37:1860–1870