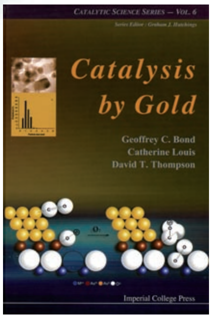
Catalysis by Gold



Vol. 6. By *Geoffrey C. Bond*, *Catherine Louis*, and *David T. Thompson*. Imperial College Press, London 2006. 366 pp., hardcover £ 51.00.—ISBN 978-1-86094-658-5

This book by Bond, Louis, and Thompson deals with a topic—catalysis by gold—that is one of the most active and growing fields in science, especially in homogeneous and heterogeneous catalysis. The book is written in a very comprehensive form, and provides a systematic review of the most important publications on heterogeneous catalysis by gold. It is clear to me that the authors have made a special effort to construct a story that is of interest not only for experienced researchers already working in the field but also for beginners and students who hope to contribute to gold catalysis. To achieve that goal, they have divided the book into 14 chapters, the first of which is an introductory tutorial on heterogeneous catalysis for beginners and students. There they present the basic concepts of chemical kinetics as applied to heterogeneously catalyzed reactions, and explain how to measure activity in reactions catalyzed by solids, and to compare the activities of solid catalysts on the basis of suitable criteria. An important aspect, which is not always appreciated by researchers less familiar with chemical engineering concepts, is the need to avoid mass-transfer limitations in order to determine the rate of the chemical transformation, the activation energy, and the heat of adsorption, so that one can correlate catalytic activity with the number and nature of active sites.

After introducing the basic kinetic concepts, in Chapter 2 the authors describe the physical properties of gold and its bulk and surface chemical properties, and put them in perspective in relation to the adjacent elements in the Periodic System. This concept is certainly relevant for understanding the interactions between gold and reactant, and the sometimes unique catalytic behavior of gold. It appears that the catalytic activity of gold cannot be ascribed to a single metallic property, but to various factors that act in concert to cause the surface interactions with the reactant molecules. The authors nicely and clearly describe the important role of relativistic effects in determining the sizes and energies of the electron shells of different elements, which accounts for characteristics of their chemical behavior that cannot be explained in any other way. More specifically in the case of gold, the relativistic effects result in an easier activation of the 5d electrons (predominance of Au^{3+}) and a much greater electron affinity and higher ionization potential for gold (formation of Au^{-}) than for copper or silver. The concepts introduced in this part of the book can explain why it is easy to generate Au^{-} and Au^{3+} species, and are very helpful in future chapters for understanding the catalytic behavior of gold for CO oxidation or as a Lewis acid catalyst. The importance of the relativistic effects on gold properties has also been reported very recently: *Nature* **2007**, *446*, 395–403. Chapter 2 ends with a brief description of the surfaces of single-crystal and bimetallic systems containing gold. Although these two subjects are treated only briefly and succinctly here, relevant references are given at the end of the chapter.Since the most important catalytic properties of solid gold catalysts are those observed for small particles, Chapter 3 elaborates on two aspects. The first one concerns methods for preparing nanoparticles of gold—gaseous clusters and particles of colloidal gold or bimetallic colloidal gold—and techniques for characterizing the nanoparticles. Techniques for the determination of particle size and structure and for measuring their optoelectronic properties include various spectroscopies, such as X-ray photoelectron, ultraviolet photoelectron, Mössbauer, X-ray absorption near-edge structure (EXAFS), infrared, Raman, UV/Visible, electron spin resonance, and anion photoelectron spectroscopies, which are described in a condensed but very clear manner. In this chapter, the authors explain that small or very small gold particles supported on carriers can "feel" the nature of the carrier, either through its effects on the size and shape of the supported particles or through electronic interactions, and therefore they discuss the influence of the support on gold particles and, reciprocally, the influence of gold particles on the support. This is important for explaining the catalytic phenomena and the behavior of gold on different supports, as discussed in the following chapters.

At this point in the book, the reader has already understood the special properties of gold, and the importance of producing gold nanoparticles to obtain active and selective catalysts. Therefore, the authors now concentrate on an excellent description of the principles and practice of supporting gold on different carriers, and methods for producing nanoparticles. They discuss the advantages and disadvantages of different preparation methods, including impregnation, co-precipitation, deposition–precipitation, and ion-exchange chemical vapor deposition.

At this stage, the reader should have a clear understanding of how to activate the support, the best conditions for gold deposition, and the importance of the nature of the starting materials, pH and temperature, and washing and activation in influencing the characteristics of the final product. It should be mentioned that although there is a greater emphasis on the methods named above, the authors do not neglect other methods, such as those based on gold in the form of dendrimers or nanoparticles prepared by photochemical, sonochemical, or beam deposition techniques. It is explained that the shape of the particles depends on the method of preparation: for example, deposition–precipitation gives hemispherical particles, whereas impregnation and photodeposition gives spheres. The shape of the particles and their size and possible electronic interactions are also influenced by the nature of the support, and the authors give explanations for these effects. All this information (supported by a large number of references) is relevant for future chapters, where the catalytic behavior of gold nanoparticles on supports is discussed.

The "gold rush" in the more recent literature started when it was discovered that supported gold nanoparticles were able to oxidize CO at lower temperatures than any other catalyst previously. This was an important discovery, since low-temperature selective oxidation of CO can be used to purify hydrogen streams for fuel-cell applications. Since then, low-temperature CO oxidation has also been used as a test reaction to evaluate success in preparing gold catalysts. Subsequently, it was found that this reaction, in combination with the techniques described earlier in the book, could give further information about the catalytic implications of the shapes of metal particles, the nature of the sites involved in activation of CO or O_2, and potential electronic interactions between gold nanoparticles and the support. The authors develop these issues in a very clear, systematic, and rigorous way in Chapters 6 and 7, following Chapter 5, in which they report on the chemisorption of the reactants involved, namely O_2 and CO_2.

All researchers interested in the selective oxidation of CO with gold catalysts, either as a test reaction or from the process point of view, will find in Chapters 5–7 an excellent and critical review, in which the authors not only present a very exhaustive literature search and discussion, but also discuss authoritative points of view and evidence. Altogether, this is a large body of information about the influence of catalyst preparation methods and of the nature of the support and of its interactions, the implications regarding the size, shape, and oxidation state of gold particles, and their CO oxidation activity and selectivity in the presence of hydrogen. Combining all this with information from "in situ" spectroscopy and kinetic studies, the authors have presented a detailed reaction mechanism. The global picture is completed by a discussion of the catalytic process and the decay of the catalyst over long periods of use.

The observation that gold nanoparticles were active and selective for low-temperature CO oxidation opened up the possibility of using this catalyst for other oxidation reactions. These are discussed in Chapter 8, starting with the industrially very important epoxidation of propylene with oxygen. For this process, gold can first catalyze the oxidation of H_2 to H_2O_2, which in turn oxidizes propylene to propylene oxide on titanosilicate supports. The effects of the nature of the gold and Ti components on activity and selectivity are discussed, with special emphasis on the synthesis of hydrogen peroxide. The authors briefly describe the oxidation of alkanes, alkenes, and cycloalkanes on gold catalysts, but concentrate in more detail on the possibilities of gold catalysts for the selective oxidation of biomass-derived products (diols, glycerol, sorbitol), and the oxidation of monofunctional alcohols to aldehydes and of aldehydes to acids.

Hydrogenation and dehydrogenation reactions with gold catalysts are also described, and the possibilities for chemoselective hydrogenation of alkynes in the presence of alkenes, or of carbonyl groups to produce olefinic compounds, are discussed. Chemoselective hydrogenations on gold have very recently generated interest for the reduction of nitro groups in the presence of olefinic carbonyl and nitrile groups (*Science* **2006**, *313*, 332–334), and this field is expected to grow.

In Chapter 10, the authors discuss the use of gold and bimetallic gold catalysts for the water-gas shift reaction. In this industrially important process, gold shows promise of being more active than Cu or Pd, probably because of its weaker chemisorption of CO. This serves as a starting point in the book to elaborate on the role of support, preparation, and activation methods on the water-gas shift activity of gold and bimetallic gold catalysts.

In Chapters 11 to 13, the authors discuss reactions of environmental importance (mainly removal of nitrogen oxides) and other reactions of interest in organic synthesis involving C-O, C-N, and C-C bond formation, among others. It should be pointed out that homogeneous gold catalysts have been widely used to catalyze reactions in organic synthesis. Such reactions and catalysts are only treated marginally in this book, in which the main emphasis is on solid catalysts. However, readers can find excellent recent reviews (*Angew. Chem. Int. Ed*. **2006**, *45*, 7896–7936) that nicely complement the results presented.

The book ends with a most interesting chapter on commercial applications of gold catalysts, which shows that this subject is not only a matter of fundamental interest but is leading to advances in transforming the knowledge acquired into solutions for industrial problems.

In conclusion, this is a comprehensive book, which builds in a rational way from the fundamentals of gold catalysis to its applications. It is an excellent guide for future work, which will contribute to the systematization of the field of gold catalysis and its rational exploration. For those whose curiosity goes further, there is an up-to-date selection of references that will help in completing the information.

I certainly recommend the book, and it should be made available in every institution working on catalysis.

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