Bridging Heterogeneous and Homogeneous Catalysis

Since 1974, when a group of experts in heterogeneous, homogeneous, and enzymatic catalysis assembled in Brussels for a symposium on the relations between their respective fields, regular and expanding efforts have been made in pursuing the goal of building bridges that—should they be successful—would both deepen knowledge of the phenomenon of catalysis and also lead to new, superior catalysts that could be designed, de novo, and utilized to solve many acute industrial, societal, economical and other problems. Among these would be cleaner technology, greener chemistry, the deployment of sustainable feedstocks as well as new ways of producing energy and harnessing solar radiation. As much energy from the sun reaches the Earth's surface in one hour as the world currently consumes as fossil fuel in one year. Moreover, it is estimated the total global power needed by 2050 will be so large that if nuclear fission alone were to meet this demand, a minimum of 10000 reactors would have to be built.

At approximately two to three year intervals international symposia on relations between homogeneous and heterogeneous catalysis (ISHHC) have been convened in places like Lyon, Groningen, Novosibirsk, Evanston, Florence, Stockholm, and Berlin, and more recently in 2013 in Sapporo. The proceedings of these symposia have been regularly published; and they constitute useful sources of reference for both novitiates and experts alike. As the last proceedings of the 16th ISHHC testifies (*Topics in Catal.* **2014**, 57, 811–1111), there are strengths and weaknesses in such publications. Whilst some authors genuinely address the task of bridging hetero- and homogeneous catalysis, others take the opportunity of "riding their hobby horses" and do little to add to the task of constructing unifying principles. Moreover, in such publications, there tends to be no strong coherent theme amongst the topics discussed.

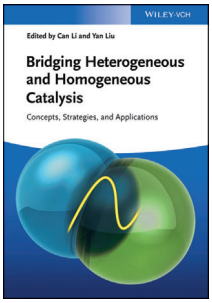
The appearance of this book, therefore, arouses much hope; and prompts one to feel that real progress in the task of bridging is chronicled here. With 30 Chinese, 4 Japanese, 2 Korean, 4 Dutch, and 2 US contributors the perspectives enunciated have inevitably a dominant Asiatic flavor, although full attention is paid to progress achieved in a world-wide context.

It is gratifying that many worthwhile attempts are made in 15 chapters to probe the relations between hetero- and homo- and enzymatic catalysts. Another chapter is devoted entirely (and thoroughly) to aspects of molecular kinetics of the Fischer–Tropsch process. Some of the contributions are spectacularly successful, notably those by Haruta and Huang and by Can Li and Yang. In the former an important distinction is made between catalysis by clusters and catalysis by nanoparticles of gold. Haruta and Huang emphasize that clusters of Au consisting of from 3 to 20 atoms are electronically and otherwise quite distinct from Au nanoparticles in the 2 to 10 nm diameter range.

Even though the chapter by Can Li and Yang (on Nanoreactors based on porous materials) is replete with good examples that bridge the hetero-homo divide, one could have wished for a little more discussion on the potential of the vast new families of nanoporous solids and metal-organic-frameworks (MOFs) that we are now witnessing. We seek in vain for the mention of the future use of MOFs in photocatalysis. Also, what of the fundamental scientific study of molecular redox catalysts incorporated into MOFs so as to ascertain the impact on catalytic performance of third and fourth coordination spheres? Such effects are vitally important in enzyme catalysis. Hitherto, in inorganic homo- and heterogeneous catalysis, it has not been possible to address this subtle question.

Finally, the addition of a simple numerical example in Can Li and Yang's fine chapter could convey that nanoporous solids, possessing surface areas ranging from several hundred to over a thousand $m^2 g^{-1}$, can serve as heterogeneous hosts to "homogeneous" (i.e. identical) catalytically active (single) sites, each identical with the others, when they are designed to be circumscribed within an area of ca 100 nm^2. This would result in a hetero-homocatalyst that has some 10^{17} active sites per gram. It is not easy to envisage a more eloquent quantitative example of the unification of homogeneous and heterogeneous catalysts. Already such systems are being used for a variety of organic syntheses; and some are highlighted in the scholarly opening chapter by Motokura, Baba and Iwasawa on "Acid–base cooperative catalysis for organic reactions by designed solid surface with organofunctional groups".

Other commendable chapters are those by Deng et al, on "Catalytic reactions in or by room-temperature ionic liquids"; which includes a lucid account of the usefulness of supported ionic liquids; by Yan Liu et al., on emulsion catalysts; and by Li and Ma on asymmetric phase-transfer catalysis in organic synthesis. The chapter by Park and Jeong on "Heterogeneous catalysis with organic–inorganic hybrid materials" is useful, but somewhat incomplete. In the two chapters that focus upon catalysis in water, no mention is made of Michel Che's definitive work in this area (see *Turning Points in Solid-State, Materials and Surface Science*, edited by K. D. M. Harris and P. P. Edwards, RSC **2007**, p. 588). Whilst it is pleasing



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to see, in Fig 9.12 a reproduction of the elegant STM work of Freund et al. (2010) on CO adsorption on supported Au nanoparticles, it is disappointing that this figure is not discussed in the light of the beautiful illustration (Figure 11.9), where it is shown that it is the atoms of Au at the perimeter interface, not those at the entire surface, that govern the catalytic performance of these metal nanoparticles.

On the whole, however, this well-illustrated text can be recommended as a valuable and up-to-date compendium of most of the bridging constructions now operational in the landscape of catalysis. It also merits comment that individuals that organize future ISHHC Symposia, or who write monographs like this admirable one, should incorporate the significant recent advances made in the resuscitated field of organocatalysis, where certain small molecules, like L-proline, mimic enzymes.

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