



Foreword

Transition-metal oxygen anion clusters (polyoxometalates or “POMs”), including heteropoly acids (HPAs), a sizable subset of POMs, are an extraordinarily modifiable and very large class of cluster compounds whose properties render them of obvious potential utility as catalysts. POMs, including HPAs, are generically resistant to oxidative degradation, most are quite resistant to thermal degradation, and in the appropriate pH ranges, they are resistant to hydrolytic degradation in solution. The reduction potential(s), solubilities, acidities, polarities, and other properties of central importance in catalysis can be varied extensively in POMs. As a consequence, the value of POMs as catalysts became apparent more than three decades ago, and several POM-based systems were commercialized as catalysts for either oxidation reactions or acid-dependent processes as long as two decades ago.

In the 10 years since I edited an issue of this journal dedicated to POMs in catalysis, several new families of POMs including giant POMs, highly reduced POMs, enantiopure POMs and multi-POM supramolecules as well as various types POM-based materials that all have applications or potential applications in catalysis have been realized. Simultaneously several fundamental experimental and computational studies on POMs have provided badly needed insight into issues of core importance in catalysis science including ion pairing, aggregation phenomena, factors influencing redox potentials, electronic structure and both electron transfer and atom transfer processes.

This volume seeks not only to update work on existing types of POM-based catalytic systems but also to provide some overarching perspectives in the form of targeted reviews in

specific areas of POM catalysis. Both homogeneous and heterogeneous systems are addressed, in part, because both types are commercially important. In addition, recent research with both soluble and insoluble POM catalysts have defined many new catalytic possibilities and posed or clarified many fundamental questions.

This first article in this issue summarizes some significant challenges in POM catalytic science. This is followed sequentially by articles and reviews addressing reactions in the following areas: homogeneous catalysis, heterogeneous catalysis, photocatalysis, and electrocatalysis. Subsequently, articles that do not fit exclusively into any of these categories but impact POM-based catalytic phenomena are presented. The last two articles are computational studies that address lead systems and phenomena central to catalysis.

I would like to thank the contributing authors and research groups in this volume for their participation. To be sure, some would have rather written a communication than an authoritative review. I also thank Dr. Yuri Geletii and Leslie Chauvin for assistance with technical editing and production of this volume.

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