Preface

Enormous progress has been made in the recent years in the synthesis of nanostructured functional materials with controlled size, shape, and functionality. These are either molecular and macromolecular materials of nanoscopic dimensions or extended tridimensional materials with nanoscopic cavities where specific functionalities are installed with controllable density and at desired locations. These materials include, but are not limited to, well-defined molecular cages, self-assembled supramolecules, dendrimers, molecularly imprinted polymers, polymers with a variety of elaborated and sophisticated structures made by living or controlled polymerization, artificial enzymes, metallorganic frameworks, porous organic frameworks, carbon nanotubes, mesoporous inorganic solids, nanocapsules, and hybrids thereof. The multiple applications that these materials offer are revolutionizing industrial sectors such as energy, electronics, sensors, biomedicine, and separation technology.

This book highlights some of the recent advances and state of the art in the use of functionalized nanostructured environments for catalysis with a particular focus on organic and metallorganic cavities. The area of catalysis within structured cavities of 3-dimensional materials such as zeolites and mesoporous oxides has not been included in this book because, though quite important in heterogeneous catalysis, it is already amply covered in other recent books. Numerous research groups show growing interest in benefitting from the nanostructure control to gain advantages or bring to light new phenomena, facing the omnipresent challenges of catalysis: higher activities, improved selectivities, catalyst stabilization, cooperativity effects, simplified protocols for cascade syntheses, better catalyst recovery, and recyclability. These advantages can be equally applied to all types of catalytic transformations, be they based on molecular complexes, stabilized nanoparticles, organocatalysts, or enzymes. The book provides contributions covering all these aspects.

Chapter "Endohedral Functionalization of Molecular Cavities for Catalysis in Confined Spaces" by Martinez et al. and Chapter "Self-Assembled Coordination Cages and Organic Capsules as Catalytic Supramolecular Reaction Vessels" by Bolliger highlight catalyst confinement in the cavity of small molecular objects, of a

covalent nature for the former and constructed via supramolecular strategies in the latter. In Chapter "Artificial Metalloenzymes," Trindler and Ward give an overview of the area of metalloenzymes, combining metal catalysis with the enzymatic scaffold ability to provide shape control and shielding. The shape selectivity concept is further developed in Chapter "Metal Complexes and Imprinted Polymers for Shape-Selective Catalysis" by Mirata and Resmini with an overview of the molecular imprinting technology and the use of molecularly imprinted polymers as catalysts and photocatalysts. In Chapter "Catalysis Inside Folded Single Macromolecules in Water," Artar and Palmans bring supramolecular interactions back to the spotlight, but this time focusing on how to create nanoconfinement via folding single macromolecules and mimicking the enzyme functionality, different from the generation of well-defined small cavities of Chapter "Self-Assembled Coordination Cages and Organic Capsules as Catalytic Supramolecular Reaction Vessels." The book continues with two chapters dedicated to star polymers topologically related to micelles. Chapter "Microgel Star Polymer Catalysts as Active and Functional Nanoreactors for Organic Reactions and Polymerizations" by Terashima and Sawamoto is focused on microgel star polymers built by atom transfer radical polymerization in a homogeneous phase, whereas Chapter "Core-Cross-Linked Micelles and Amphiphilic Nanogels as Unimolecular Nanoreactors for Micellar-Type, Metal-Based Aqueous Biphasic Catalysis" by us with collaborators presents related catalytic nanoreactors made by reversible addition–fragmentation chain-transfer radical polymerization in emulsion. Aspects such as biphasic catalysis and recycling are highlighted in these chapters. Then, Caminade et al. present recent advances made with catalytic dendrimers in Chapter "Catalysis Within Dendrimers." Finally, we conclude the book with a survey, in Chapter "Site Isolation for Non-orthogonal Tandem Catalysis in Confined Nanospaces," of catalyzed tandem processes achieved in one pot by site-isolating incompatible catalysts in different compartments of the same nanoreactors.

I hope that the selected material provides a balanced and useful reference in this rapidly expanding area to all readers: a useful introduction for the nonexperts, useful references for the practitioners, and especially perspectives and opportunities for future development for those who wish to embrace this area in their future research work.

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