Multicatalyst System in Asymmetric Catalysis

JIAN ZHOU

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PREFACE

The past 50 years have witnessed vast achievements in asymmetric catalysis, which has reached to such a level that excellent enantioselectivity for many reactions can now be finally achieved, given intensive screenings and necessary substrate modification. On the other hand, if existing catalytic asymmetric protocols are under scrutiny by the criterion of the ideal synthesis, most of them have ample room for further improvement in terms of atom utilization, energy consumption, and waste generation. For example, the modification of substrates with an activating group or bulky shielding group is a widely adopted strategy to achieve the desired reactivity and stereoselectivities, but such a manipulation unfortunately decreases the synthetic efficiency, if the introduced auxiliary is essentially unnecessary for the final optically active products. Therefore, a long-standing challenge confronting chemists in the field of asymmetric catalysis is to meet the guidelines of ideal synthesis, namely to struggle for ideal asymmetric catalysis. Undoubtedly, chiral catalysts play a crucial role in turning this goal into reality, and the exploitation of new catalyst systems is indispensable for improving the efficiency of known protocols, and for realizing asymmetric transformations currently unattainable. However, the discovery of new powerful chiral catalysts is by no means a piece of cake, as evidenced by the fact that although enormous efforts have been devoted in the past 50 years, only a handful of privileged chiral catalysts are available that are capable of realizing excellent stereoselectivities in more than 10 kinds of reactions. In addition, there in no way exists a single privileged chiral catalyst that can solve all the problems. Accordingly, to achieve ideal asymmetric catalysis not only requires the development of new privileged chiral catalysts, but also demands strategies to make the best of known enantioselective catalysts.

The multicatalyst system catalysis, on the basis of the combination of multiple distinct catalysts with at least a chiral one, has recently emerged as a promising strategy to tackle the challenges in achieving ideal asymmetric catalysis. As the victory of battles builds on the coordination of all the soldiers, no matter ordinary or supersoldiers with capabilities beyond normal limits, so does the remarkable efficiency of the multicatalyst system originate from the cooperation of distinct multiple catalysts, no matter chiral or achiral. The "two heads are better than one" effect, realized by a multicatalyst system, can be classified into three major types: (1) asymmetric cooperative catalysis (simultaneous activation of distinct reaction partners); (2) asymmetric double activation catalysis (double activation of one substrate); and (3) asymmetric assisted catalysis (the generation of an enhanced catalytic species via catalyst interaction). By any of the three activation models, the energy barrier of the reaction is lowered down to a more effective extent than by monocatalysis. In addition, multicatalyst systems are in particular attractive for the development of tandem reactions, which essentially mimic the multienzymatic system that Nature employs in the complex molecule synthesis.

In 2010, I was invited to write a focus review on the recent advances in multicatalyst promoted asymmetric tandem reactions (*Chem. Asian J.* **2010**, *5*, 422–434), which witnessed the rapid development of this area in the past several years. Intrigued by this topic, Dr. Jonathan T. Rose, the senior editor of Wiley-VCH, encouraged me to develop this topic into a book. Because of our research interest in this field, I regarded this as a golden opportunity to get an in-depth understanding of this emerging area, and spent 3 years collecting and assorting literatures, while preparing the draft. During the process, it came to my attention that although this area has received much attention nowadays, there is indeed thirst for a book to provide a comprehensive definition, discussion, and summarization about the application of multicatalyst system in asymmetric catalysis, as all the known review articles just focused on one aspect of this research field. For example, the use of a certain additive to greatly improve the reactivity and stereoselectivity of an asymmetric reaction is well-documented, but there is no proposed standard to distinguish the additive-enhanced catalysis from multicatalyst system catalysis. In addition, almost all the known review articles focus on introducing asymmetric cooperative activation realized by multicatalyst system, and pay little attention to the other two important types, asymmetric double activation catalysis and assisted catalysis. Therefore, based on my 15 years' experience in the field of asymmetric catalysis, I leave no stone unturned to give a thorough introduction about the function, classification, and application of multicatalyst systems in asymmetric catalysis, and special attention is paid to differentiate multicatalyst system catalysis from multifunctional catalysis or additive-enhanced catalysis. Accordingly, unless to show the basic concepts, only literature reports with sufficient control experiments to demonstrate the crucial role of each catalyst component of the multicatalyst system are selected and introduced.

This book begins with discussion on the criterions of ideal asymmetric catalysis and the challenges on the way to this lofty goal, and proposes the development of new activation models and new chiral catalysts as a promising strategy to achieve ideal asymmetric catalysis. The following chapter introduces the known models of

activation in both nucleophiles and electrophiles, summarizes the early examples of multicatalyst promoted asymmetric reaction, discusses the basic activation models provided by multicatalyst system, presents the differences between multicatalyst system catalysis and multifunctional catalysis, proposes a standard to distinguish multicatalyst system catalysis from additive-enhanced asymmetric catalysis, and finally, highlights some representative additive-enhanced asymmetric reactions, which might be helpful for readers to compare and strengthen their understanding.

The following chapters are organized into interlinked sections and will benefit readers to grasp the advantages of multicatalyst catalysis, which include: asymmetric multifunctional catalysis (Chapter 3); asymmetric cooperative catalysis (Chapter 4); asymmetric double activation catalysis (Chapter 5); asymmetric assisted catalysis (Chapter 6); asymmetric catalysis facilitated by photochemical or electrochemical method (Chapter 7); multicatalyst system realized asymmetric tandem reaction (Chapter 8); waste-mediated reactions (Chapter 9); and multicatalyst system mediated asymmetric reactions in total synthesis (Chapter 10).

This book is timely and reflects the latest achievement in this area till 2013, which would be helpful for players in this field to have a quick overview and to design new related chemistry. Importantly, it provides wonderful opportunities for readers outside this field to be aware of this important emerging area and attract more students and chemists to engage in this research field. Moreover, the knowledge and information will also provide an educational opportunity for the public to learn that asymmetric catalysis can be done in "greener" ways to make useful enantioenriched substances, as well as to change their perceptions of organic synthesis as a dangerous, toxic, hazardous, and pollutive science.

I would like to avail myself of this opportunity to thank the Wiley-VCH editorial staff, in particular to Jonathan T. Rose for proposing and encouraging me to write this book, and to Amanda Amanullah, Ho Kin Yunn and Shalini Sharma who are of precious help for the development of this project. I also thank my students Yu-Hui Wang, Miao Ding, Yu-Lei Zhao, Xiao-Ping Yin and Fu-Ming Liao for their kind help in proofreading.