



RECOVERABLE and RECYCLABLE CATALYSTS

Editor Maurizio Benaglia

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Recoverable and Recyclable Catalysts

Edited by

Maurizio Benaglia

Department of Organic and Industrial Chemistry, University of Milan, Italy



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Recoverable and Recyclable Catalysts

Preface

Why anyone should read a book about recoverable and recyclable catalysts? The reason is already contained in the three words of the title.

Catalysis represents a frontier field of research, the concept of catalysis being one of the key features of modern chemistry where a substoichiometric amount of compounds is used to produce large amounts of other compounds. Catalysis is one of the twelve principles of Green Chemistry: a process based on a catalytic methodology is already “green” by definition, since it is clearly stated that “catalysts are preferable to stoichiometric reagents.”

Recoverable is also a fundamental word for the chemistry of the future, where terms like sustainability or low environmental impact will become more and more important. So a recoverable catalyst will generate less waste and will be a key step toward the development of more efficient processes.

Recyclable clearly refers to a fundamental topic for the industry, the economy and the efficiency of the process, and it represents the link between the research in academy and industry. What is better for a company than the possibility to reuse again and again the same catalyst?

The development of recyclable catalysts represents a fascinating challenge that may be tackled from several different points of view; it is indeed a real interdisciplinary field, where pure chemistry is deeply bound and connected to material science, or engineering and where even business and economy-related issues play an important role in determining the planning, the design and the realization of a project in the area. It is a field where many technologies and opportunities are offered to successfully realize an easy recoverable and, what is more important, reusable catalytic system.

In this book the first chapter introduces the reader into the world of recyclable catalysts; written by a world wide recognized authority in the field it presents general principles which should be considered when a study in this area will be conducted and it offers a key to critically approach the reading of the other chapters where different methodologies used to realize a modern, efficient process involving recyclable systems will be discussed. After this introductory chapter in the first three chapters the somehow “traditionally” exploited techniques to realize heterogenized catalysts are presented, where different supports, inorganic and organic materials, soluble or insoluble polymers are discussed. In the following six chapters other methodologies, alternative to the traditional strategies, are illustrated, from the use of ionic liquids or supercritical CO₂ until the perfluorinated systems. Thermomorphic catalysts as well as polymeric, or self supported catalytic systems are all relatively new areas of investigation of potential enormous growth. In the last chapters some “new” topics in the field of recoverable catalysts are presented, such as the development of reusable organic catalysts, and the use of micro encapsulated catalysts or the employment of

new devices and “enabling technologies” like flow and membrane reactors, mini and micro reactors that represent the future of the synthetic chemist, which will have to be applied to catalysis as well in the next years. The final chapter represents an attempt to make a few general considerations on the immobilization process, and by using two case studies, one organometallic species and one organocatalyst, to try to compare the behaviour of the same catalytic species anchored to all different supports.

I am really happy with the list of authors which have agreed to contribute to the volume and I am honoured to act as editor of a book whose chapters were delivered all by worldwide recognized experts in the area, which are universally considered in many cases the real pioneers in their own field. This gives a strong historical background of great authority to the chapters, which are anyhow principally devoted to discuss the recent, more important achievements in the field and in this way significantly leaning to the future perspectives and challenges in the area. For the neophyte in the field the book wants to be an easy to consult guide, that introduces the reader in the very complex topic of the recoverable and recyclable catalysts, giving an idea of how many possibilities and how many challenges are still out there to be tackled with new ideas and new approaches. On the other hand, for the experts in the field, the book wants to be the occasion to establish some general, important milestones, as starting points from which the future investigations will move towards new objectives but within a rigorous, well established scientific methodology, necessary for the design of new catalytic systems but also for the correct evaluation of the obtained results. In any case the real goal of the book is to promote new achievements in the field, to stimulate the interest of more scientists in entering and working in a very multidisciplinary area of research; the book wants to be a “catalyst” for the development of new recyclable catalysts.

My personal wish is that the reader will enjoy the consultation of this book as much as I personally enjoyed in reading all chapters and editing a volume where a really multifaceted and stimulating chemistry is presented, where creativity, fantasy and courage emerge as qualities required to the modern chemist which wishes to successfully work in this field.

Maurizio Benaglia

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Contributors

Maurizio Benaglia	Department of Organic and Industrial Chemistry, University of Milan, Milan, Italy
David E. Bergbreiter	Department of Chemistry, Texas A&M University, College Station, Texas, USA
Johan C. Brandt	School of Chemistry, Cardiff University, Cardiff, UK
Sascha Ceylan	Institut für Organische Chemie, Leibniz Universität Hannover, Hannover, Germany
Zhuo Chai	Shanghai Institute of Organic Chemistry, Shanghai, China
Hung-Ting Chen	Department of Chemistry, Iowa State University, Ames, Iowa, USA
Tamilselvi Chinnusamy	Institut für Organische Chemie, Universität Regensburg, Regensburg, Germany
David J. Cole-Hamilton	EaStCHEM, School of Chemistry, University of St. Andrews, St. Andrews, Fife, Scotland
Franco Cozzi	Department of Organic and Industrial Chemistry, University of Milan, Milan, Italy
Simon L. Desset	EaStCHEM, School of Chemistry, University of St. Andrews, St. Andrews, Fife, Scotland
John A. Gladysz	Department of Chemistry, Texas A&M University, College Station, Texas, USA
Petra Hilgers	Institut für Organische Chemie, Universität Regensburg, Regensburg, Germany
Qiao-Sheng Hu	Department of Chemistry, College of Staten Island and the Graduate Center of the City University of New York, Staten Island, New York, USA
Andreas Kirshning	Institut für Organische Chemie, Leibniz Universität Hannover, Hannover, Germany
Victor S. Y. Lin	Department of Chemistry, Iowa State University, Ames, Iowa, USA
Wenbin Lin	Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, USA
David J. Mihalceik	Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, USA

Jun Ou	Department of Chemistry, The University of Hong Kong, Hong Kong
Oliver Reiser	Institut für Organische Chemie, Universität Regensburg, Regensburg, Germany
Tibor Soós	Institute of Biomolecular Chemistry, Chemical Research Center of the Hungarian Academy of Science, Budapest, Hungary
Patrick H. Toy	Department of Chemistry, The University of Hong Kong, Hong Kong
Brian G. Trewyn	Department of Chemistry, Iowa State University, Ames, Iowa, USA
Thomas Wirth	School of Chemistry, Cardiff University, Cardiff, UK
Jianliang Xiao	Department of Chemistry, Liverpool Centre for Materials and Catalysis, University of Liverpool, Liverpool, UK
Lijin Xu	Department of Chemistry, Renmin University of China, Beijing, China
Gang Zhao	Laboratory of Modern Synthetic Organic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China

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1

The Experimental Assay of Catalyst Recovery: General Concepts

John A. Gladysz

*Department of Chemistry, Texas A&M University,
College Station, Texas, USA*

1.1 Introduction

Congratulations. You have a well-placed interest in catalysis, and specifically in recoverable catalysts. Over the next several hundred pages of this book, you will encounter many types of recovery strategies and cleverly designed catalysts. You could have begun with these chapters, which many would say are more exciting and contain the ‘good stuff’. But instead, you have started here, where some thinly veiled sermonizing awaits. Please persevere, and ‘be converted’ to the ranks that strive for the highest quality in research. It is not difficult to carry out rigorous quantitative studies of recoverable catalysts. But many researchers fall far short. Serious deficiencies can even be found in some references cited in the individual chapters.

A catalyst accelerates the rate of a chemical reaction, and is left unchanged by the reaction.¹ Given this definition, the most obvious way to measure the efficacy of catalyst recovery is by the rate of a subsequent reaction cycle. If the catalyst is not completely recovered, the rate must be slower. The yields of products isolated from preparative reactions are most commonly determined gravimetrically, and catalyst recoveries can in principle be assayed analogously. However, this is not as general, as analyzed further below. For example, the very small amounts of catalysts used in many reactions virtually preclude