

Chapter 1

Background of Combinatorial Catalyst Development

Catalysis has had considerable impact on the chemical industry for more than a century. In spite of its long-lasting practical application, scientific breakthroughs are still needed in terms of its fundamental foundations. This is true particularly for catalyst development, although significant contributions to the fundamentals of catalysis were recognized. Highly esteemed awards illustrated this only recently. In the field of heterogeneous catalysis various recognitions were awarded: the 1998 Wolf Prize to G. Ertl and G. Somorjai, the 2007 Nobel Prize to G. Ertl and the 2007 Priestley award to G. Somorjai. Also in homogeneous catalysis significant scientific progress was achieved as manifested through the 2001 Nobel Prize to W.S. Knowles, Ryoji Noyori, and K. Barry Sharp and the 2001 Wolf Prize to Ryoji Noyori.

For a full understanding of heterogeneously catalysed reactions the relations between synthesis and characterization of catalytic materials, and their catalytic performance with respect to activity and selectivity are required (Hinrichsen *et al.*, 1997; Ertl *et al.*, 1983, Ertl and Huber 1980; Grass 2008). Within the 21st century the main focus will be mostly on selectivity from a practical point of view for saving chemical resources and for avoiding harm to the environment from undesirable and poisonous products.

For an *a priori* design of catalysts only during the last decade, a few promising results have been obtained (Vang *et al.*, 2005, Neurock 2003; Jacobsen *et al.*, 2002); this is, in general, still impossible for multi-step reactions, for which selectivity plays the major role.

The industrial application of catalysis includes chemicals production and refinery operations as well as environmental protection (e.g. towards clean air and clean water) and energy-related (e.g. hydrogen production) processes; the latter two applications of catalysis are recently receiving increasing attention. In producing chemicals, usually at least one reaction step is driven by catalysis. About 80% to 90% of all chemical processes are based on catalysis and approximately 90% of this proportion involves the application of heterogeneous catalysts. Bulk chemicals are produced via either single- or multi-step chemical reactions in the refining and chemical industry including the production of primary chemicals for the synthesis of pharmaceuticals. Single-step processes include the Haber-Bosch process for the synthesis of ammonia, the oxidation of ammonia to NO as an intermediate towards nitric acid, and the oxidation of SO₂ to SO₃ for obtaining sulphuric acid. Multi-step processes, which consist of parallel and consecutive reaction steps, are among others reforming and cracking of crude oil-derived hydrocarbons, desulphurization, selective oxidation of alkanes and olefins to their oxygenates, hydrogenation of unsaturated hydrocarbons, and the synthesis of acrylonitrile and acrylic acid and of fine chemicals. Catalyst applications for environmental protection include those for automobile exhaust-gas purification, and for energy-related purposes such as hydrogen production via electrochemical catalysis for energy storage from solar plants. These selected examples illustrate the variety of heterogeneously catalysed chemical reactions.

The estimated annual value of all solid catalysts produced amounted in 2006 to about 13 billion euros per year worldwide and is expected to increase (not accounting for the present financial and economic crisis) to 16 billion euro in 2010 (Fischer 2009). The value of the catalyst market may be roughly subdivided to its different applications as shown in Table 1. The value created by these catalysts is in the order of about 100 to 1000 times as high. (Ertl *et al.*, 2008).

The commercial success of catalysis has been quite impressive and one might expect that catalysis is a mature science since it has now been industrially applied on a large scale for more than a century. However, this is not the case, as has been indicated above. Today, the *a priori* design of a catalyst for high product selectivity of complex (multi-step) reactions is mostly not yet possible. Fundamental knowledge still needs

Table 1.1. Approximate values of catalyst market (Fischer 2009).

Area	% of market value	
	2006	2010
Environment	33	(39)
Chemical and petrochemical	24	(19)
Refining	27	(18)
Polymerization	22	(24)

to be supplemented by empirical experience for discovering new catalysts for such purposes in a rather time-consuming procedure (see Chapter 2). However, one may anticipate that in about one to two decades, i.e. by about 2020 to 2030, it should be possible to predict the performance of a catalytic material in many situations on the basis of theory-driven approaches and accumulated fundamental knowledge.

At present, progress in catalyst design still very often relies on trial and error, even when partly applying fundamental knowledge. Therefore, statistical and machine-learning approaches are used to put the development process on a reproducible and rational basis. Such methods require a multitude of properly designed and collected experimental data for statistical analysis and deriving quantitative relationships between catalytic performance and the physical and chemical properties of the catalysts. Screening large amounts of materials, derived from combining different components, for their catalytic performance, requires suitable high-throughput technologies to obtain numerous, sufficiently reliable catalytic data over a limited time span by applying high-throughput technologies for preparation and testing.

Apart from experimental and dedicated theoretical methods, combinatorial computational chemistry approaches also exist (Koyama *et al.*, 2007), which are based on *ab initio* molecular orbital calculations. More details about these methods have been recently briefly summarized (Baerns and Holeňa 2008).

Combinatorial development of heterogeneous catalysts has proven to be a means of reducing the time for finding improved or new catalytic materials. The advantage of combinatorial catalyst development derives from appropriate, computer-aided design of experiments and their rapid execution using high-throughput technologies. Moreover, data evaluation

and data mining play an important role in the combinatorial development of catalytic materials. These issues are the main focus of the present monograph.

It is, however, noteworthy that conventional methodology is still being successfully used in many cases (Trimm 1980; Stiles 1987; Le Page 1987; Richardson 1989; Becker and Pereira 1993; Wijngaarden *et al.*, 1998; Morbidelli *et al.*, 2001). A comprehensive and up-to-date overview of many aspects of preparation, characterization, and testing of solid catalysts, which is valid not only for conventional methodology but also for combinatorial catalyst development, has recently been published (Ertl *et al.*, 2008; Hutchings and Vedrine 2004).

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