CHINA PARTICUOLOGY Vol. 3, No. 6, 383–394, 2005

● ***Review & Perspective***

CATALYST TECHNOLOGY DEVELOPMENT FROM MACRO-, MICRO- DOWN TO NANO-SCALE

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Abstract Catalyst and catalytic process technology has been an ever-growing field that involves chemical engineering, chemistry, and material science. A number of excellent review articles and books have been published on the subject. In this work, the author reviews the evolution and development of catalyst products with multi-scale methodology. The catalyst technologies are classified into three levels, macro-scale (reactor size), mini- and micro-scale (catalyst unit), and nano-scale (catalyst intrinsic structures). Innovation at different scales requires different sets of expertise, method, and knowledge. Specific examples of significant impact to practical application are used to illustrate technology development at each scale. The multi-scale analysis enables clear delineation of technology components and their relationship for a catalyst product and catalytic process. Manipulation of catalyst structures at nano-scale to increase intrinsic activity and/or selectivity is considered of large potential for future catalyst product development. Recent research results on Cu-CeO_2 and Au-CeO_2 composite catalysts for air pollution control and hydrogen production are used to show how novel catalytic properties can be discovered by unique combination of different but common materials at the nano-scale.

Keywords multi-scale, nano-scale, catalyst, composite, ceria, copper, gold

1. Introduction

Catalytic technologies are critical to present and future energy, chemical process, and environmental industries. Conversion of crude oil, coal and natural gas to fuels and chemical feedstock, production of a variety of petrochemical and chemical products, and emission control of CO, hydrocarbons, and NO, all rely on catalytic technologies. Catalysts are also essential components of electrodes for fuel cells that use either solid oxide ionic or polymeric proton electrolyte. Drivers for development of advanced catalysts include (i) production of high value products with inexpensive raw materials, (ii) energy-efficient and environmentally-benign chemical conversion processes, (iii) increasingly stringent environmental regulations, and (iv) low-cost catalysts such as with reduction or replacement of precious metals.

Catalyst material, catalysis, reactor design and catalytic process constitute a broad but inter-related research field. A number of excellent books, treaties, and review articles have been published addressing almost every aspect of the catalyst science and technology. For example, Satterfield (1991) provided a comprehensive introduction to solid catalysts for significant industrial application. In the present work, the author attempts to elucidate product development of solid catalysts from a different point of view by classifying catalyst technologies at different dimensions or scales.

Li and Kwauk (2003) proposed a multi-scale methodology for analysis of complex systems in chemical engineering, and demonstrated it as an insightful approach toward revealing and quantifying detailed flow structures of gas-solid fluidized beds. Three kinds of multi-scale methodology, descriptive, correlative, and variational, were presented. Catalyst technologies are qualified as a complex system. Its complexity is not only limited to materials or compositions and structures, but also includes simultaneous occurrence of mass transfer, heat transfer, and chemical reaction. Describing and classifying catalyst technologies at different scales is a first step in applying the multi-scale methodology but is a step change to the way in which catalyst technologies are traditionally viewed. The catalyst technologies are often discussed or reviewed on the basis of specific subjects or piece-by-piece, while an actual working catalyst or catalytic process is an innovative integration of many technology components (materials, chemistry, chemical engineering). From his own experiences in research and industrial practice, the present author has found that multi-scale methodology can be fairly helpful in understanding the relationship of different technology components with reactor performance and in clarifying critical issues in problem-solving of a particular catalyst or catalytic process.

The present discussion of catalyst technologies is based on the packed bed reactor, which is commonly used in industrial catalytic processes. However, discussions at particle scale or at nano-scale are applicable to other reactors such as fluidized beds. Fig. 1 shows a working catalyst bed/reactor broken down into three different levels, macro-level (reactor-scale, 10 mm – 10 m in reactor diameter), mini- and micro-level (particle size scale, 3 mm to 10 nm), and nano-scale (active catalyst site or structure scale, atomic to a few nm). Table 1 lists the specific objective and set of specialty at each scale. Clearly, catalyst research and development belongs to a multi-disciplinary field. Synthesis or preparation, and characterization involve a great amount of materials science

Table 1 Catalyst product design and engineering at different scales

Scale	Purpose	Material Aspect	Chemical Engineering Aspect
Macro-level (reactor-scale)	Overall conversion performance: yield, productivity, lifetime	Catalyst bed structure, packing method, crush strength, attrition	Hydrodynamics and pressure drop, bulk mass and heat transfer, reactor model
Mini- and micro-level (Catalyst particle or unit scale)	Effectiveness factor of individual reaction	I. Catalyst particle shapes or forms II. Catalyst distribution, pore size and pore size distribution	Pore diffusion mass transfer, reaction kinetics
Nano-level (Catalyst structure scale)	Intrinsic catalytic activity and selectivity	Catalyst composition, active structure or configuration	Quantum chemistry calculation, molecular reaction dynamics, new sciences

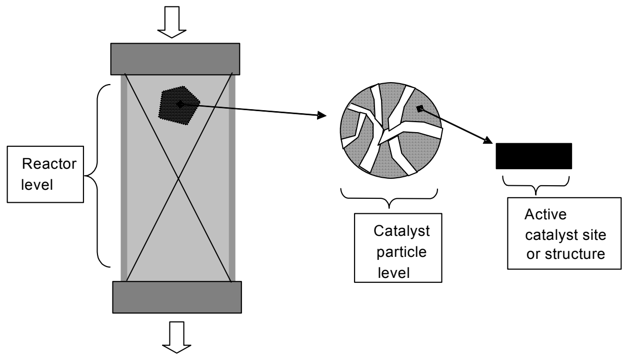

Fig. 1 Breakdown of catalyst bed/reactor into three different scales.

and processing expertise as well as solid-state chemistry knowledge. Reaction testing and application development comprise core chemical engineering subjects, hydrodynamics, mass and heat transfer, chemical reaction engineering. Mechanistic understanding requires reaction kinetics and surface chemistry.

In a top-down approach, multi-scale analysis enables decomposition of a complex catalyst bed/reactor into individual technology components, and helps identification of their relationship/interaction. The method is useful both for troubleshooting/improvement of a commercial catalytic process and to interpretation of laboratory or pilot plant testing results. Technology components of all three scales are embedded in a given catalytic bed/reactor. If one wants to determine and understand "intrinsic" activity and selectivity of a catalyst material, one has to take into account implication of parameters and variables at the other two scales to the experimental results.

In a bottom-up approach, multi-scale analysis is helpful to thinking through research and development plan of a new catalyst material. If a new material structure or composition is discovered for excellent catalytic activity and/or selectivity, in order to develop it into an actual product, one has to make effective design and engineering of the catalyst material at particle size and reactor level to realize its intrinsic performance.

A great amount of technology innovation and scientific understanding has been achieved at the reactor and particle scales. However, to a large extent, the catalyst structure or composition is still treated as a black box. Discovery of active catalyst composition and/or structure is needed for dramatic improvement to catalytic processes in the future. For solid (or heterogeneous) catalysts, single atom or molecule does not comprise a catalyst as compared to homogeneous catalysts, and large crystalline size gives small surface area. Thus, material preparation and characterization at nano-scale is necessary to pursue this research endeavor. Furthermore, molecular reaction dynamics and quantum chemistry calculation should become an important tool as reaction engineering calculation has contributed to catalyst research and development at reactor and particle size levels.

2. Design and Engineering at the Macro-Scale — Reactor Level

Design and construction of catalyst beds at reactor level has been well developed. At this scale, the catalyst product or bed design becomes an integral part of reactor design. A variety of catalyst beds or reactor configurations have been used in commercial processes. Dautzenberg and Mukherjee (2001) presented a recent review of different reactor configurations including membrane reactors. Fig. 2 illustrates a few of different packed bed or fixed bed designs. A reactor vessel uniformly loaded with a number of catalyst particles (or units) is a simple, ideal configuration. The actual reactor for large-scale industrial application, however, often encounters limitations in pressure drop, heat transfer, mass transfer, and catalyst contamination.

Most of catalytic reactions are either endothermic or exothermic. Thus, heat transfer is critical to control reaction temperature and achieve optimum reactor performance. For example, temperature run-away can result in catastrophic failure for selective oxidation reactions of hydrocarbons. As a result, tubular reactors are resorted to for solving this problem. In the tubular reactor, catalysts are loaded into a reactor tube of small diameter (2 to 20 cm) with heat exchange fluid flowing around the shell side.

Graded catalyst beds comprise several layers of catalysts of different sizes and/or different catalytic functions, depending on specific application. It offers several performance attributes. Different steps of an overall catalytic conversion process may be conducted in the same reactor vessel. Catalyst contaminants carried in by feedstock can be contained in the front bed. By gradually decreasing catalyst particle size along the reactor depth,