

# Toward Clean Technology:

## How High-Throughput Heterogeneous Catalysis Helps

Refining and chemical conversion relies on heterogeneous catalysts, chemically complex formulations with ill-defined structures and mechanisms of action. The parameter space needed to optimize such catalyst systems is quite large, and traditional methods of synthesis and testing are manual, slow, and inefficient.

For more than a decade, Symyx has collaborated with industry-leading chemical and energy companies to develop automated, high-throughput technologies for synthesizing and testing large numbers of materials for catalytic and other functional applications. Today, Symyx's ground-breaking work in this

field is giving refining and chemical companies leverage as they respond to the need for "clean technology." Organizations seeking to develop innovative new technologies to lower the emission of carbon dioxide and other undesirable by-products during the manufacture and use of energy, chemicals, and materials will need to begin by adapting the existing heterogeneous-catalyst-based processes that drive the modern refining and chemical conversion infrastructure. This article describes Symyx's achievements in the development of high-throughput workflows for heterogeneous catalysis and describes how this workflow was recently applied to optimize a "cleaner" catalyst system.

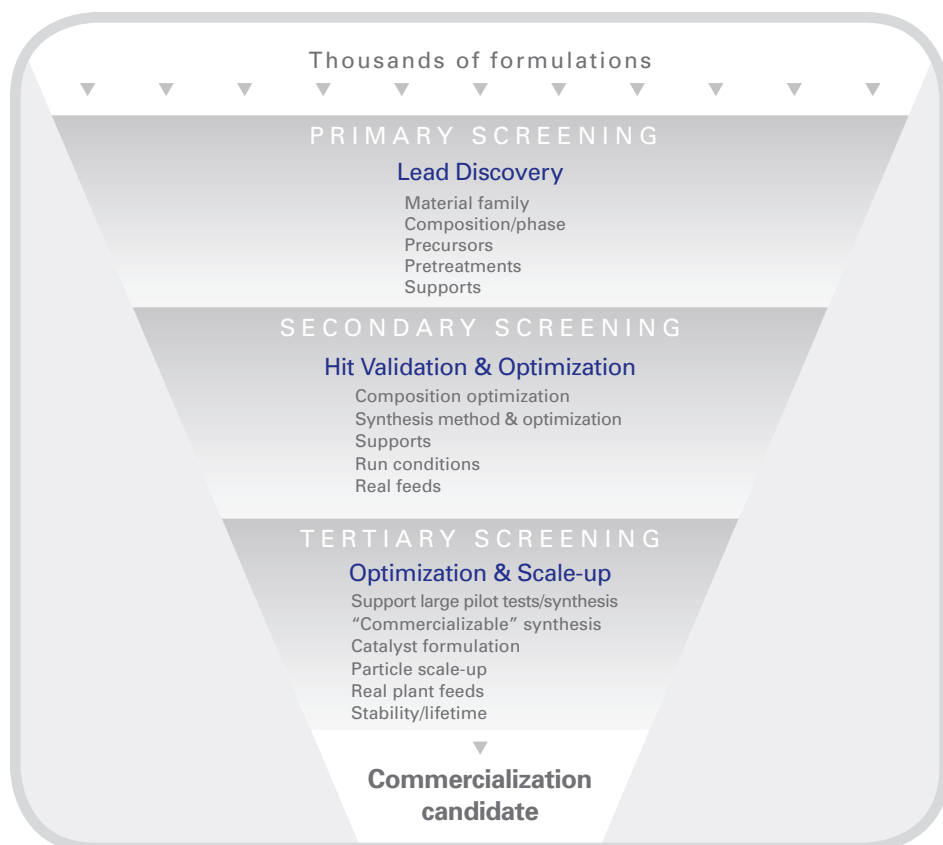


Figure 1: Catalyst discovery and development research proceeds through three phases that encompass specific functional activities.

### High-Throughput Materials Discovery

High-throughput methods were developed in the 1980s to improve the efficiency of drug discovery and optimization. These methods included high-dimensional experimental techniques, such as "split-pool" synthetic procedures where mixtures of thousands of compounds were created on beads; parallel synthesis to produce a collection of related organic compounds known as a "library;" and new property screening technologies that allowed scientists to sort through large collections of potential leads efficiently and, increasingly, precisely.

The application of high-throughput methods to heterogeneous catalysis proceeds in three distinct phases (see Figure 1). In primary screening, multiple families of materials that logically could perform the desired catalytic transformation are qualitatively evaluated; families unlikely to work are eliminated in order to focus on "hits," new classes of materials that show promise for a specific application. Successful primary screens explore a broad experimental space and may include thousands of experiments. Primary screening generally favors proxy analytical tests over full

property characterization and requires a careful balance between throughput and precision to achieve resolutions that minimize the chance of false positives and, more importantly, false negatives. Hits from primary screening are ranked and evaluated further in secondary screening workflows, which assess the viability of hits as development candidates and further optimize catalyst formulation for activity and selectivity. At this stage, the synthetic methods and screening technologies employed must closely mimic the various commercial processes used across relevant industries. Advanced secondary screening methods are often at least as precise as conventional laboratory methods and balance both speed and precision.

Finally, optimized leads enter the third phase of development: scale-up and commercial testing in pilot or semi-works plants. High-throughput methods have shifted more catalyst development work from the pilot plant to the lab. This enables scale-up to, in turn, shift its focus to those catalysts with the greatest probability of success and frees plant resources to address late-stage questions, such as the effect of recycle or time on efficacy, and to produce customer qualification batches, greatly reducing the number of costly pilot plant runs required.

### Synthesis and Screening Workflows: Unit Operations and Architecture

The most simple, effective high-throughput workflow for chemical catalysis comprises four unit operations: liquid/solid handling robotics, parallel batch reactors, chemical archives, and analytical testing stations (see Figure 2). Symyx has developed methods and technologies in each of these areas and offers critical expertise to integrate these unit operations and execute a variety of early-stage catalyst discovery and optimization programs. While this workflow has been well deployed for discovery and optimization of olefin polymerization catalysts<sup>1</sup> and for route selection and process optimization of fine chemicals, it has been more difficult to apply to continuous processes such as those used in petroleum refining. Additionally, heterogeneous catalyst performance depends on several variables, such as composition, morphology, and size, which themselves vary based on the synthesis method employed.

High-throughput heterogeneous catalyst synthesis and screening workflows, therefore, require specialized robotics and parallel, continuous systems that closely mimic their commercial counterparts. For synthesis, Symyx has developed high-throughput units for

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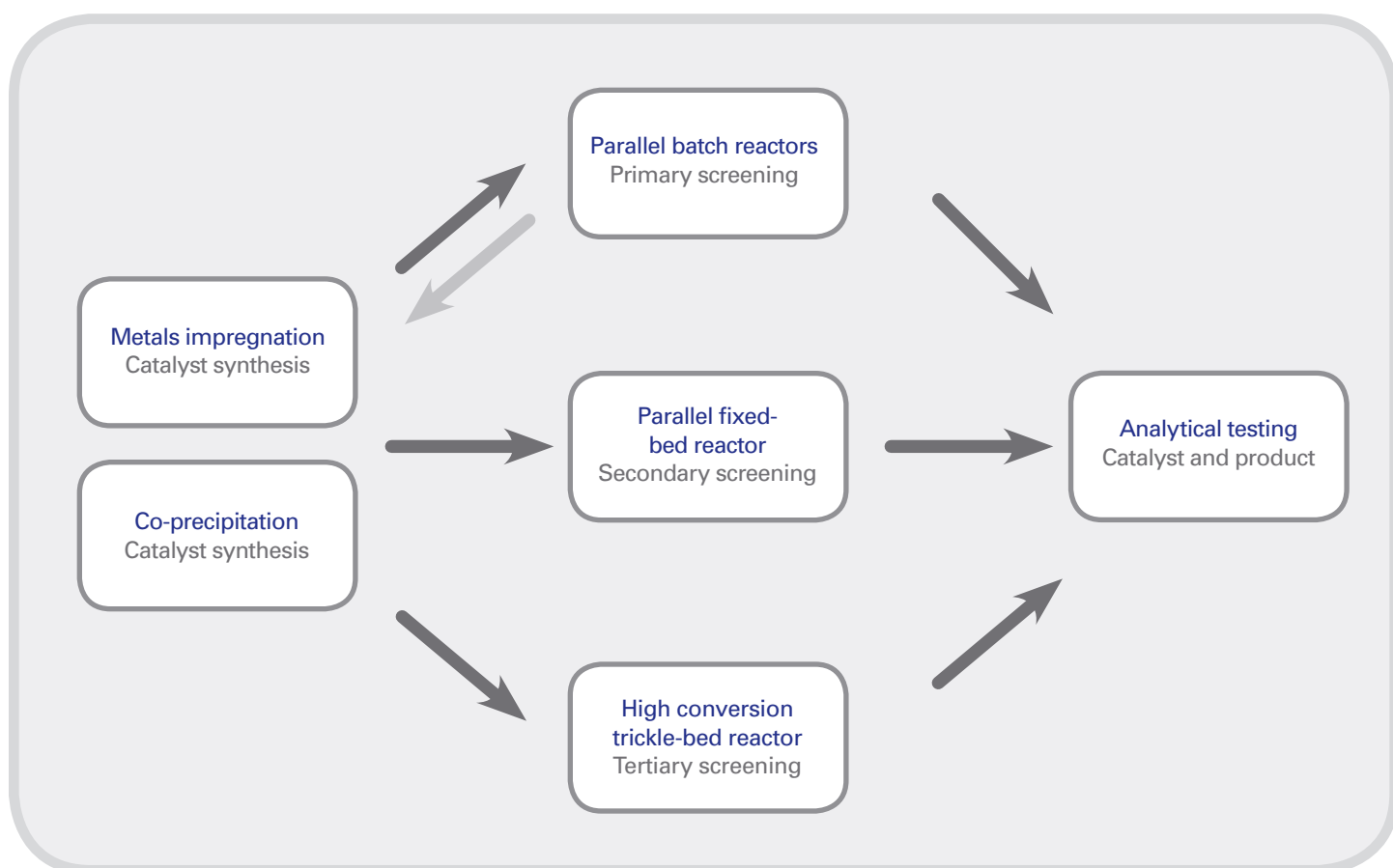
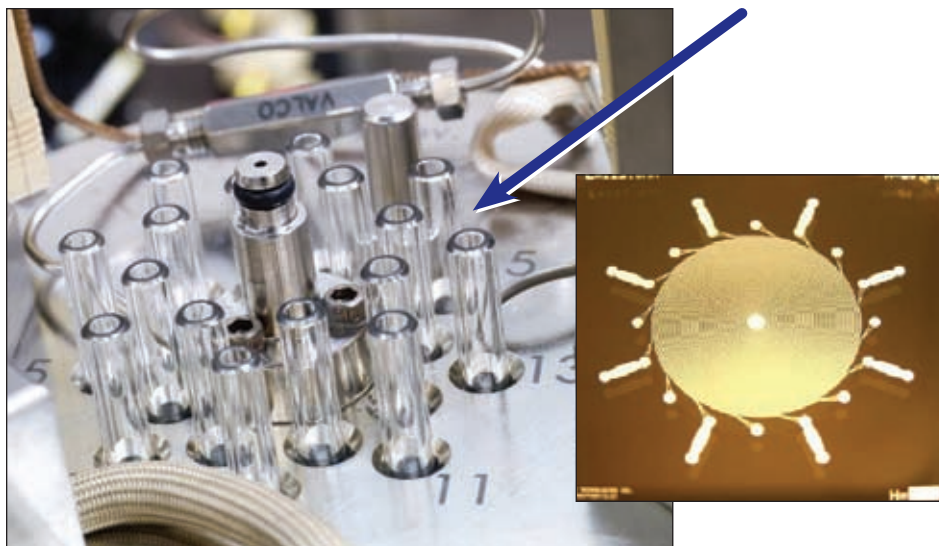


Figure 2: The Symyx heterogeneous catalysis development workstream incorporates batch reactors for screening thousands of formulation families, fixed-bed reactors for optimizing catalysts under flow-through conditions, and trickle-bed systems that can run high conversions.



*Figure 3: The Symyx Parallel Fixed-Bed Reactor makes continuous, fixed-bed technology accessible outside specialized laboratories through two unique elements. The microfluidic flow splitter (right) replaces capillaries to ensure uniform feed control to each reactor. The reactors are surrounded with a pressurized atmosphere that enables a variety of materials, including quartz (left, at arrow), to be used as a reaction vessel. The design helps to minimize leaks by reducing the pressure delta between the reaction tube and surrounding atmosphere.*

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parallel impregnation, co-precipitation, hydrothermal reactions, and solvent evaporation. All common catalyst preparation techniques are available in high throughput, as is supporting equipment for parallel grinding, washing, and sizing workflows.

The dominant commercial process in refining deploys heterogeneous catalysis in a continuous, fixed-bed process. Several laboratory-scale microreactors have been developed that take into account design principles such as catalyst and reactor size and shape, surface area-to-volume ratio, hydrodynamics, and heat and mass transfer. These microreactors, however, are mechanically complex, difficult to operate, and may not produce the highest quality data.

Symyx has made continuous, fixed-bed technology more accessible and applicable by, for example, using microfluidics technology to develop a flow restrictor on a chip that splits a single feed (gas, liquid, or gas/liquid phases) into the individual channels of the parallel fixed bed reactor at a constant flow rate (see Figure 3). Further mechanical improvements engineered by Symyx have reduced the number of seals and potential leak sources, facilitated loading and maintenance, and enabled testing at higher pressures and temperatures and a wider range of space velocities. Several workflows comprising this technology have been validated and applied to a broad spectrum of refining, petrochemical, and chemical application areas including selective oxidation, oxidative dehydrogenation, ammoxidation, acetoxylation,

hydrogenation, isomerization, and emissions abatement hydrodesulfurization.

### **Optimizing Heterogeneous Catalysts Using Secondary Screening Methods**

Today, thanks to many years of engineering progress and research at Symyx, high-throughput workflows can be used to optimize existing, highly evolved catalyst systems and to discover new applications in mature, well studied catalyst families. Such workflows stand to be a boon to companies seeking to develop clean-energy alternatives. A recent high-throughput research program at Symyx illustrates the utility of this approach. Strict regulation of sulfur emissions worldwide has challenged refiners to develop “cleaner” hydrodesulfurization (HDS) catalysts. Ideally, HDS catalysts would selectively reduce sulfur-containing compounds, such as alkyl thiophenes, without hydrogenating olefins, which not only raises the sulfur level, but reduces fuel quality (octane number). One of the most advanced selective HDS technologies, SCANfining, was developed by ExxonMobil using a selective catalyst commercialized with with AkzoNobel (now Albemarle) and is currently used in over 30 refineries worldwide.

The Symyx program aimed to develop improved naphtha HDS catalyst technologies for high octane number gasoline production. The catalyst synthesis workflow included automated precursor preparation and dispensing followed by serial impregnation and optional wash and reduction steps. Workflow hardware comprised a metal impregnation station for catalyst synthesis and a 48-channel fixed-bed reactor for catalyst evaluation. Products were analyzed online using gas chromatography with FID and SCD detection to quantify hydrocarbons and olefin- and sulfur-containing species. The experiments were performed as follows:

- 1) Synthesized each library of 48 catalysts using incipient wetness impregnation of pre-sized supports with soluble precursor solutions.
- 2) Loaded dried and sized solids into 3 mm–40 mm vials and into the reactor for testing.
- 3) Sulfided catalysts *in situ* with virgin naphtha, and initiated HDS testing using a naphtha feed. Catalysts remained on stream until they reached steady-state performance. Catalyst performance was then compared in reference to a commercial HDS catalyst.

Approximately 500 new catalyst formulations were tested at several space velocities and temperatures during a six-month discovery effort. Some 5,000 data points were evaluated for these catalysts. Tests yielded a new catalyst that was 50% more

selective and 30% more active for sulfur removal than the commercial reference (see Figure 4).<sup>2</sup> Additionally, the presence of standard catalysts in each of the libraries that were run allowed quantification of the performance and quality of the data produced by Symyx's 48-channel reactor. Over a one-year period and ten reactor loadings (more than 200 data points) at a constant 87% conversion, the selectivity of the reference was  $11.8\% \pm 1.2\%$ . This clearly indicates that the Symyx reactor system produced data of much higher quality than that generally produced by secondary screening high-throughput reactors.

### Summary

Clean-technology investments span a broad spectrum of possible technological solutions. Chemical catalysis and surface science, however, will play a defining role in the transition to an economically attractive, environmentally friendly, and more sustainable energy, fuels, and chemicals industry. In particular, high-throughput methods, such as those developed by Symyx and its collaborators, will enable and accelerate our ability to evaluate and adopt new technological strategies.

**For further reading on improving reaction efficiency and clean technology using high-throughput heterogeneous catalysis see:**

C. Brooks, et al., "High-throughput discovery of CO oxidation/VOC combustion and water-gas shift catalysts for industrial multi-component streams," *Topics in Catalysis*, 38 (1-3), 195-209 (2006).

S. Cypes, et al., "High-throughput screening of low temperature CO oxidation catalysts using IR thermography," *Comb Chem High Throughput Screen*, 10 (1), 25-35 (2007).

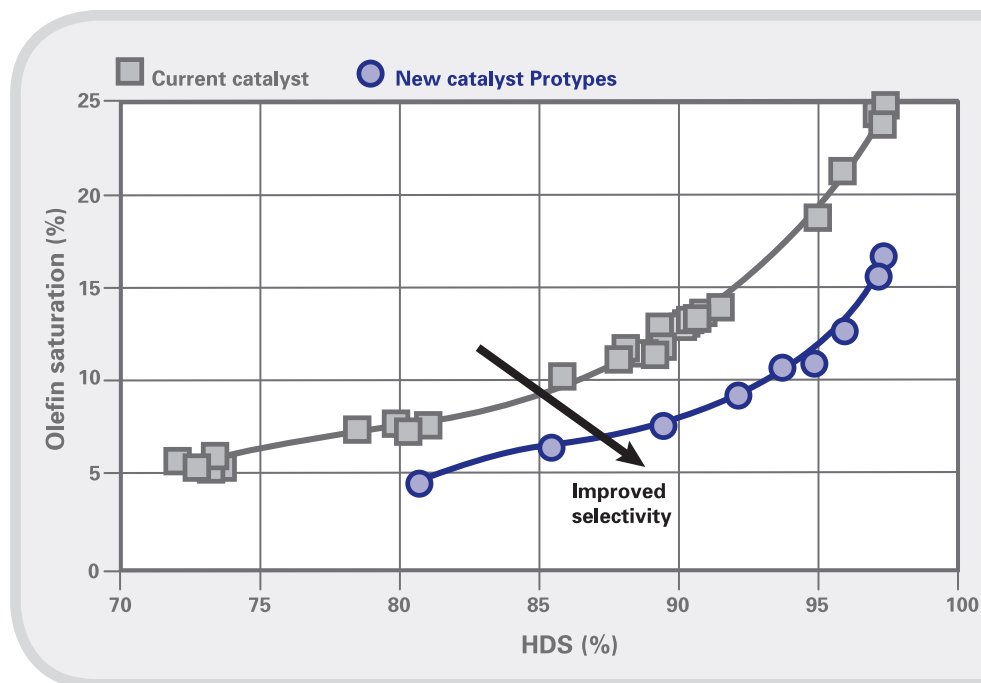


Figure 4: Efforts to produce an improved hydrodesulfurization catalyst produced new catalyst prototypes (blue) with higher selectivity and better sulfur removal than the current catalyst (gray).

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<sup>1</sup> V. Murphy, "High-throughput approaches in olefin polymerization catalysis" in *High-throughput Screening in Chemical Catalysis: Technologies, Strategies, and Applications*, ed. A. Hagemeyer, P. Strasser, A. Volpe (Wiley VCH Verlag GmbH, Weinheim), 299-312 (2004).

<sup>2</sup> J. S. Beck, "Advanced catalyst technologies and high-throughput experimentation at ExxonMobil," *Symyx Symposium 2007—Productive Science*, Boston, MA, May 15-16, 2007.



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