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Encouraging innovation in catalysis

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Abstract

Catalysis plays a critical role in virtually every industry. Often it is the key to making an entirely new technology or breathing new life into an otherwise, mature technology. In addition to the continued needs for productivity improvements, environmental drives and heightened industrial safety add a new aspect to the importance of catalytic innovation.

ABB Lummus Global, along with its many industrial partners, has a well-established, track record of fostering innovation in its many technologies. These innovations take form in many ways: (a) catalyst design, (b) advanced materials, (c) new process concepts, (d) engineering advances, and (e) novel uses of high throughput screening.

Moving projects through the "technology pipeline" used to be done by brute force–using an army of scientists and engineers. Today that luxury no longer exists, and industry must embrace creative approaches to leverage their resources and accelerate the development and commercialization of new technology. This paper presents specific examples of innovation at Lummus. These examples will, once again, reinforce the point that catalytic innovation is clearly an important vehicle to continued advancement of society.

Keywords: R&D productivity; Innovation; Catalysis

1. Introduction

Industrial R&D, unlike traditional academic research projects, focuses on commercialization as the final objective. Economic pressures almost inevitably push the researchers to accelerate the timescale of the development effort. In addition to this ever-present management mantra, the last 20 years or so have seen the shrinking of R&D budgets as an overriding phenomenon. Quite often one has heard the painful and puzzling words "Do more with less." Painful because it often involves downsizing and increased productivity demands upon the individual. Puzzling because it seems to violate a thermodynamic law, or at least, simple logic. Given this backdrop of the current industrial R&D environment, one can immediately see the heightened importance of innovation. Moreover, since more than 90% of all industrial processes are catalytic in nature, fostering innovation in catalysis is an essential component for increasing the flow in the technology pipeline and, ultimately, adding value to business and society.

This paper will show that nurturing innovation in catalysis is an effective way to boost R&D productivity. To encourage innovation, five aspects will be discussed:

1. Business pull
2. Technology push
3. Advanced tools
4. Industrial alliances
5. University collaborations.

2. Business pull

Many scientific advances often begin with a specific need in mind. The electric light bulb and automobile are two classic examples. Since the early days of electricity and automotive transportation, the needs have continuously evolved. Many of the business needs today revolve around environmental regulations. In petroleum refining, gasoline and diesel fuel quality are changing in many dramatic ways.

To put the ultra-clean fuels "business pull" in perspective, let's look at the general composition of gasoline and some of the major gasoline quality issues. Fig. 1 shows the composition of gasoline. This pie chart is for U.S. gasoline, but

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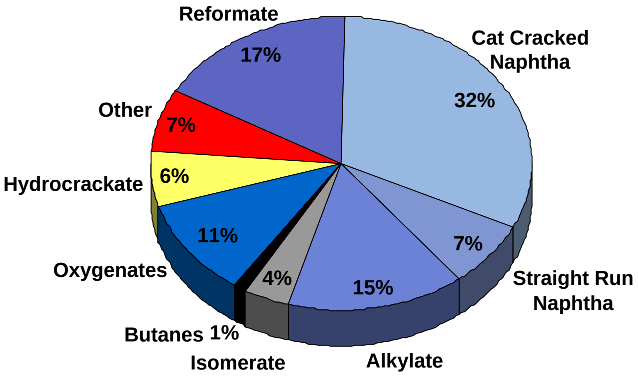


Fig. 1. Composition of US gasoline.

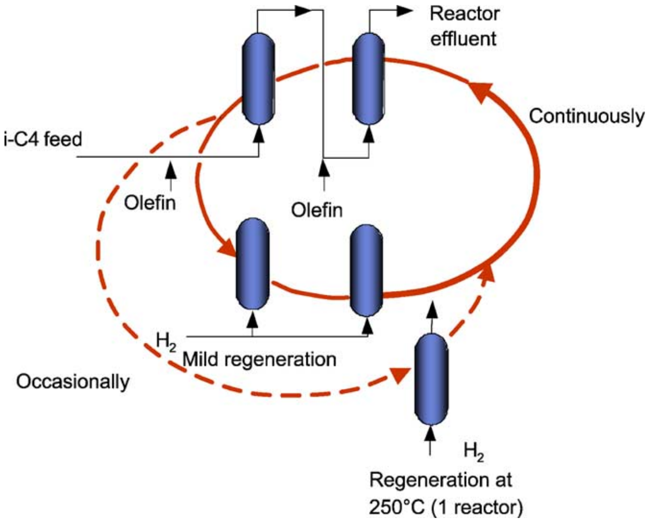


Fig. 3. Typical AlkyClean^{SM} process reactor scheme.

the components and issues are similar worldwide. Of the various components, FCC gasoline (i.e. cat cracked naphtha) is the largest piece of the pie and is also the major source of sulfur. The U.S. Environmental Protection Agency (EPA) has developed a toxicity equation that quantifies the impact of the key pollutants. Sulfur is, by far, the primary pollutant problem. Reducing sulfur not only directly reduces SO_x emissions, but also improves the efficiency and effectiveness of catalytic converters, thereby also lowering NO_x and CO emissions. A second major gasoline component, reformate, is a major source of high octane due to its high aromatics content. Unfortunately, the aromatics include benzene, which is toxic, and therefore there is regulatory pressure to reduce it. Our joint venture partner, CDTECH®, has developed catalytic distillation processes that effectively and efficiently remove benzene and sulfur from these two gasoline streams.

Let’s move on along the pie chart to oxygenates (e.g. ethers, such as MTBE, ETBE, TAME). In the last decade we have seen the use of oxygenate additives as a route to lower the CO emissions in gasoline. Unfortunately, one major oxygenate, MTBE, is being restricted in some countries due to its toxicity and water solubility. The opportunity here is to identify cost-effective routes to other oxygenates, such as ethanol.

The next significant piece of the pie is isomerate. Here, we mean products of C_5 and C_6 isomerization. These isoparaffins are “clean” (i.e. sulfur- and aromatics-free) and raise the pool octane. The two major catalysts used in isomerization are halogenated aluminas and zeolites, both with noble metal. Higher activity versions of these bifunctional catalysts should raise the iso-to-normal product ratio and thereby boost octane. Another paraffin component that could be a candidate for isomerization is *n*-heptane, but due to its reactivity, *n*-heptane is preferentially cracked to propane and *iso*-butane via conventional catalysts, instead of isomerizing. A recent breakthrough was achieved in this area at MIT in an ABB-sponsored research project. Here, a noble metal/mixed metal oxide catalyst has been shown to be very active and selective for isomerization and polyisomerization [1]. As it evolves, we expect this to be an important new process in the ultra-clean fuels arena.

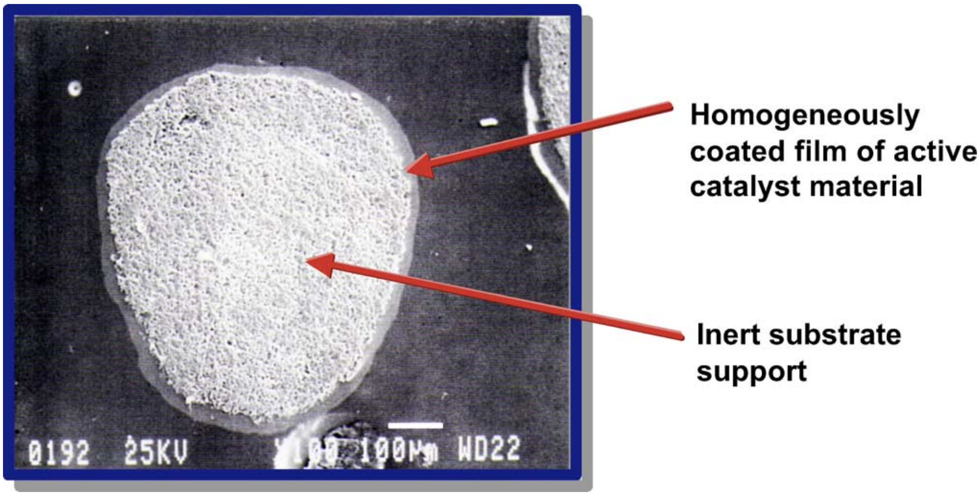


Fig. 2. Thin film catalyst for alkylation.

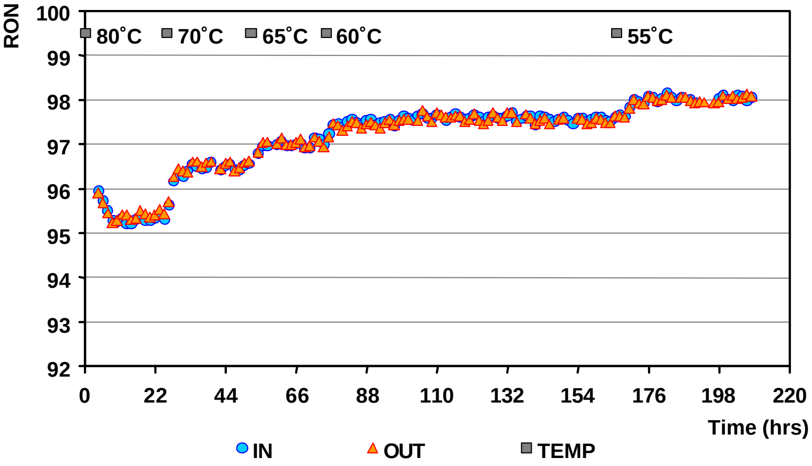


Fig. 4. Typical pilot plant results: cyclic operation with optimized catalyst, RON vs. time.

The last major piece of the pie is alkylate. Composed primarily of C_8 isomers, alkylate has virtually no toxicity and is very high in octane. As such, it could be the ideal gasoline on its own, and demand for this environmentally friendly fuel is growing. However, conventional alkylation processes use hydrofluoric or sulfuric acids, both of which pose serious safety and handling problems. To mitigate this problem refiners have long sought solid acid catalysts for alkylation—one of the great elusive challenges of refining. ABB Lummus Global, together with Akzo Nobel and Fortum Oy, have developed a solid acid catalyst process called the AlkyClean^{SM} alkylation technology.

R&D activities related to the AlkyClean technology [2] began in 1997 with investigating the merits of thin film catalysts (Fig. 2). A thin layer of active catalyst is deposited selectively on a solid support, such that the catalytic materials do not penetrate the support [3]. The thinness of the highly porous catalyst layer creates a very low diffusion barrier. As a consequence, formation of catalyst deactivating heavy by-products is suppressed, which leads to enhanced catalyst life and better product selectivity. Pursuing the understanding gained with the thin film concept, a more practical, robust zeolite catalyst with controlled morphology was developed [4]. Fig. 3 is a schematic representation of the AlkyClean reactor system. The two reactants, i-C_4 and olefins (primarily butylene), are fed to multi-staged reactors. Since the catalyst deactivates quickly, other reactors are used in the reaction sequence. While the catalysts in the first reactors undergo a mild H_2 regeneration, the other reactors are brought on stream. This sequence continues for hundreds of cycles, and occasionally an extra reactor is swung into service while one reactor undergoes a higher temperature H_2

Fig. 5. Reactor section of AlkyClean^{SM} demonstration plant.

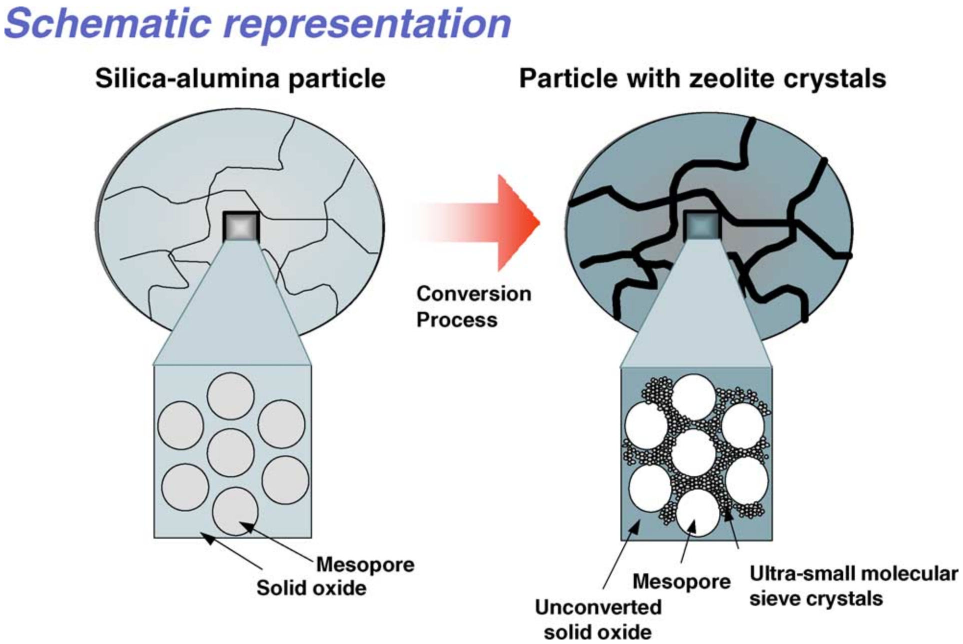


Fig. 6. Novel zeolite synthesis procedure: “Dry-Synthesis”.

regeneration. Fig. 4 shows typical pilot plant data [2]. The AlkyClean process is now in the final stages of development, and a large-scale demonstration unit is currently being operated in Porvoo, Finland (Fig. 5). Operation of this unit has enabled us to confirm the overall soundness of the new technology. It is anticipated that the AlkyClean technology can successfully be introduced into refineries in the near future.

3. Technology push

Technology push can take many forms. These can include catalyst design, reactor concepts, and new process designs. One concept under development at Lummus is in zeolite synthesis. Specifically, the innovation is morphology control to achieve ultra-small particles that have little or no mass transfer limitation. Intraparticle mass transfer limitations, important in fast reactions, often occur in industrial applications where conversion levels are high. The Lummus innovation deals with a zeolite synthesis procedure that we call “dry synthesis” [5,6]. Its name is based on the fact that the liquid reactants (e.g. caustic, water, and organic directing agent) are added to the solid reactant (e.g. silica–alumina) at or below the incipient wetness point. Hence, the solid appears dry.

Fig. 6 is a schematic representation of “dry synthesis” [7]. On the left side is a preformed silica–alumina particle having mesopores within the solid oxide. On the right side, we see the finished product. It retains the gross morphology of the original particle, and most of the silica–alumina has been converted to ultra-small molecular sieve crystals. In Fig. 7, the pore size distribution is shown for the dry synthesis (left) versus a conventional zeolite synthesis (right). Note that the

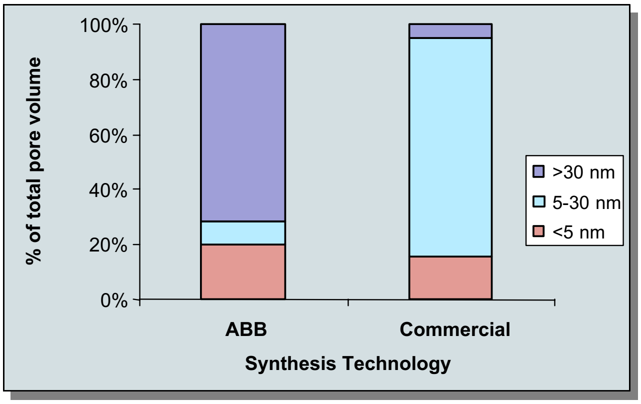


Fig. 7. Pore size distribution of two catalysts.

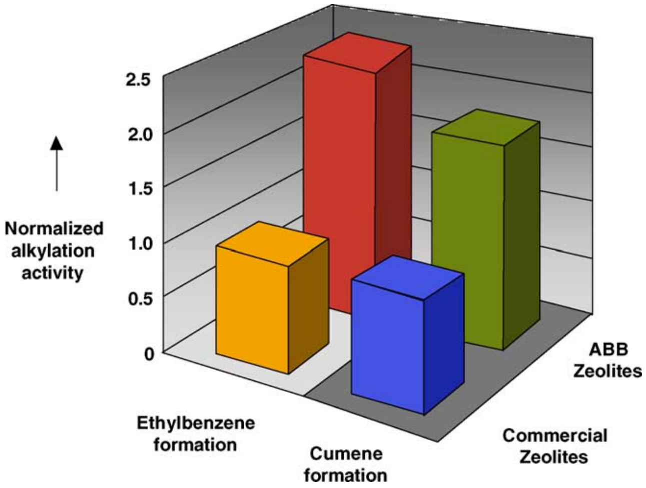


Fig. 8. Aromatics alkylation: comparison of catalyst performance.

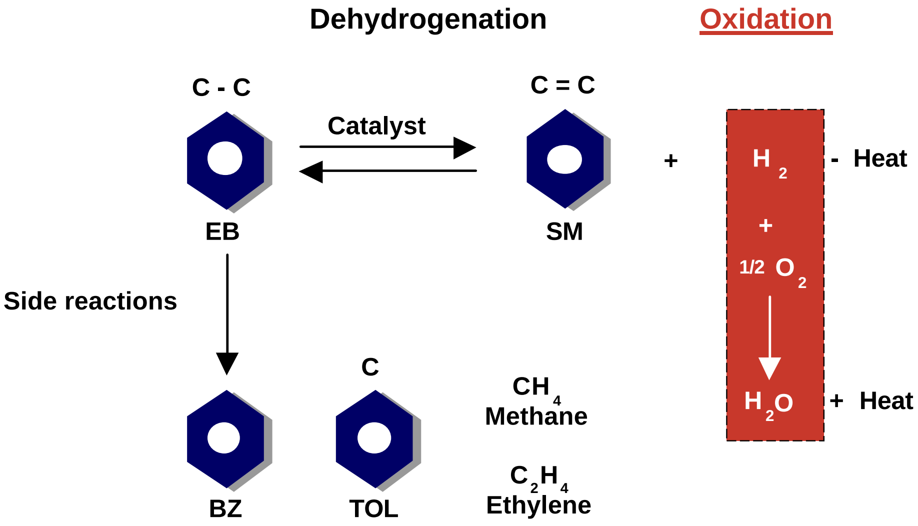


Fig. 9. Process chemistry with oxidative reheat.

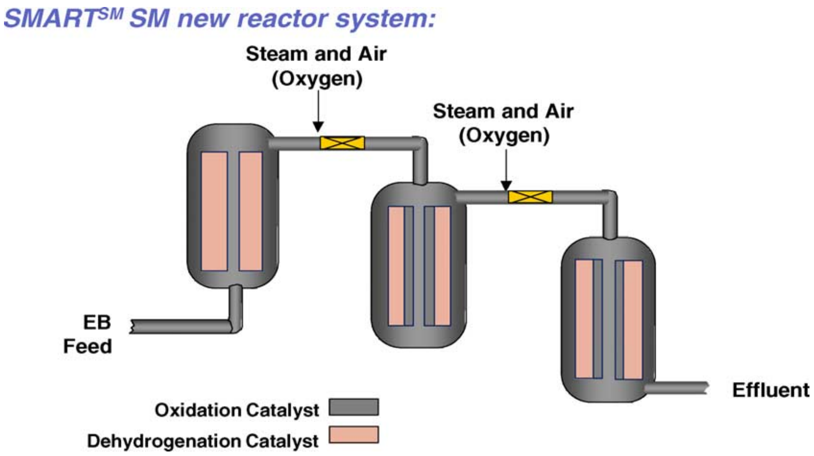


Fig. 10. New reactor system of Styrene Monomer Advanced Reheat Technology.

dry synthesis product has an unusually high amount of large mesopores (i.e. pores > 30 nm). The pore size distribution is critical in many catalytic reactions because the mass transfer is impacted by a series of composite resistances. Two examples of improved catalytic performance are shown in Fig. 8. Here, the reactions shown are aromatics alkylations, i.e. forming ethylbenzene and cumene. In this bar chart, the reference activities are normalized to 1.0. For the EB process, the "dry synthesis" zeolite shows an activity is more than double the reference catalyst. For cumene production, the "dry synthesis" zeolite also shows a significant activity advantage versus the reference catalyst. These examples are merely for illustrative purposes; many other benefits of "dry synthesis" zeolites have been demonstrated.

Another technology innovation revolves around the ethylbenzene (EB) dehydrogenation process that forms styrene—the starting monomer for polystyrene. Fig. 9 shows the overall reactions involved in styrene monomer (SM) production. Dehydrogenation of EB to SM is a highly endothermic reaction, and as the temperature drops in an adiabatic reactor, the yield becomes less favorable due to thermodynamic equilibrium. Other undesirable by-products include benzene, toluene, and light gases like methane and ethane. The new technology concept is to employ a second reaction—simple oxidation of hydrogen to water—to add heat to the system and raise the overall average reactor temperature, thereby boosting the overall conversion. One method to add heat is shown in Fig. 10, where intrareactor reheat is employed in stages. This process design, known as SMART (Styrene Monomer Advanced Reheat Technology), has been commercialized in five plants.

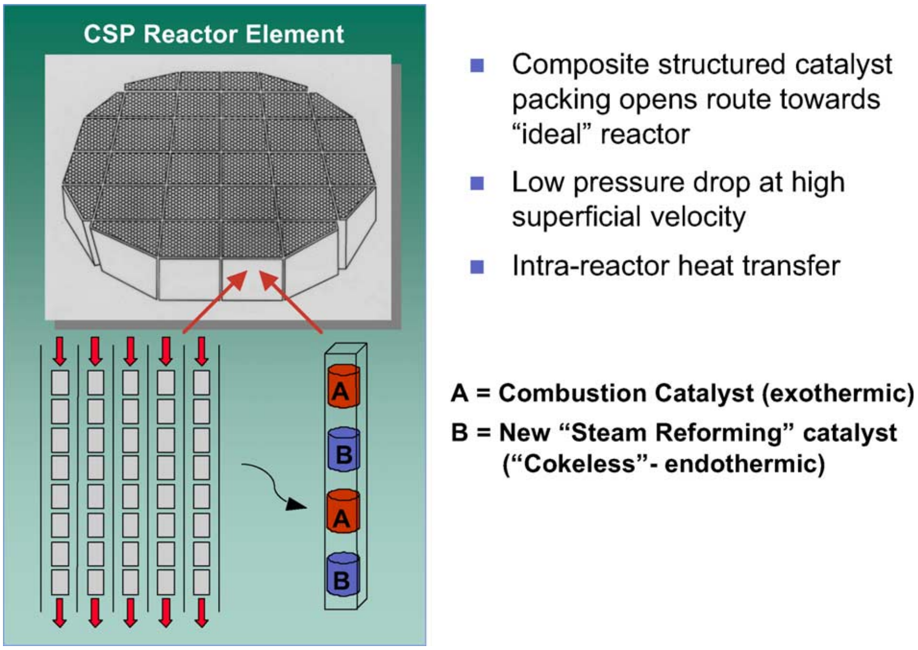
Steam reforming:

$$CH_4 + H_2O \rightleftarrows CO + 3\,H_2 \qquad \Delta H^{\circ}_{298} = +\ 206\ \text{kJ/mol}$$

***Catalytic Partial Oxidation*:**

$$CH_4 + \tfrac{1}{2}\,O_2 \longrightarrow CO + 2\,H_2 \qquad \Delta H^{\circ}_{298} = -\ 36\ \text{kJ/mol}$$

Fig. 11. Steam reforming and catalytic partial oxidation of methane.



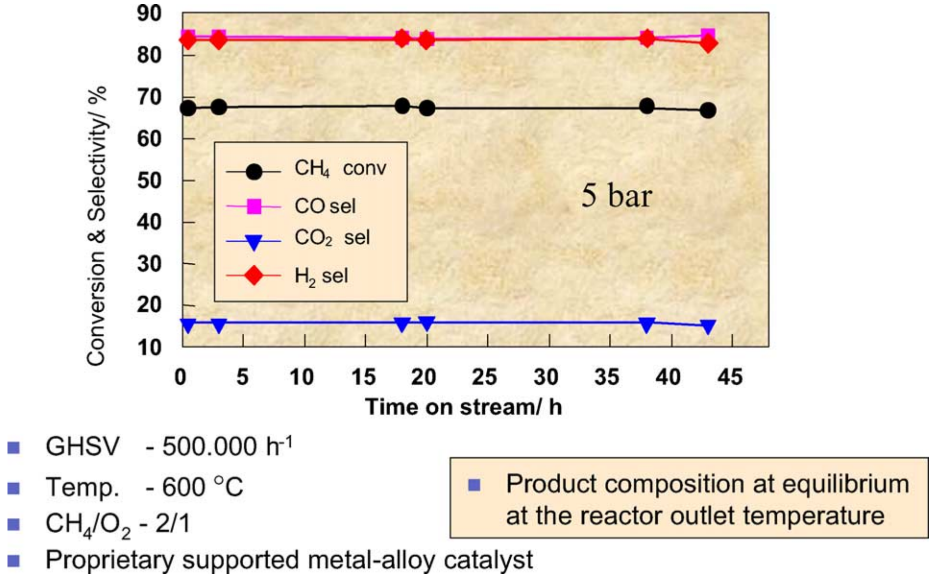
- Composite structured catalyst packing opens route towards “ideal” reactor
- Low pressure drop at high superficial velocity
- Intra-reactor heat transfer

A = Combustion Catalyst (exothermic)

B = New “Steam Reforming” catalyst (“Cokeless”- endothermic)

Fig. 12. Composite structured packed (CSP) reactor with CPO catalyst system.

The same principle can be applied to steam reforming of methane, the primary method of hydrogen manufacture as well as syngas production. As shown in Fig. 11, this reaction is highly endothermic. The “heat input” approach can now be applied via catalytic partial oxidation (CPO) of methane. With CPO, part of the methane is combusted to generate the energy to drive the endothermic steam reforming reaction. One innovation here is actually two independent concepts melded together to provide a synergistic benefit. The first innovation is a novel Lummus reactor concept called composite structured packing (CSP) (Fig. 12). The second innovation is a true breakthrough—a “cokeless” steam reforming catalyst that was the result of an ABB-sponsored collaborative project with the National University of Singapore (NUS). CSP, with its high void fraction and associated low pressure drop, is ideally suited for high superficial gas velocity applications such as this. In the preferred configuration, each reactor element has an alternating packing of the two catalysts, i.e. the combustion catalyst followed by the cokeless steam reforming catalyst. The catalyst proportions can be varied to optimize the temperature band. Fig. 13 shows the performance in a CPO



- GHSV - 500.000 h^{-1}
- Temp. - 600 °C
- CH_4/O_2 - 2/1
- Proprietary supported metal-alloy catalyst

- Product composition at equilibrium at the reactor outlet temperature

Fig. 13. Typical catalytic partial oxidation results.

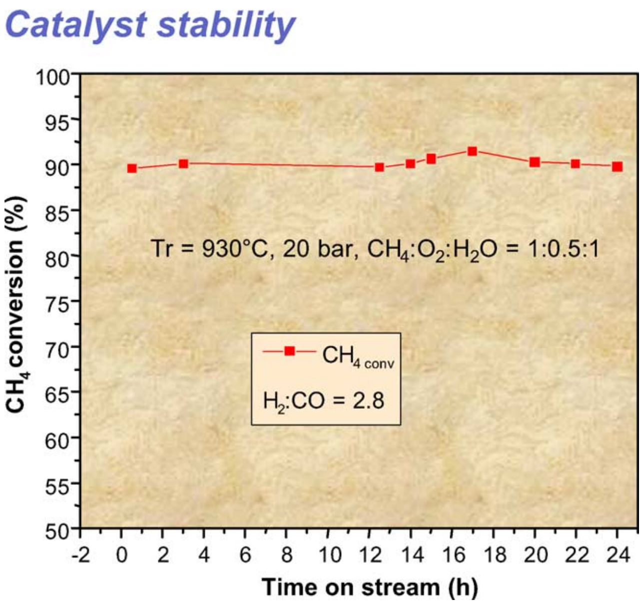


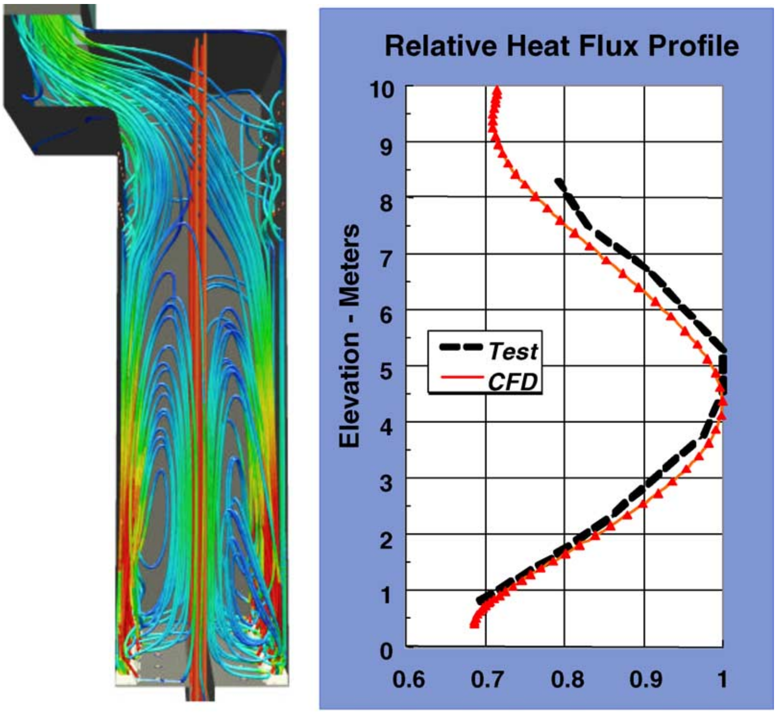
Fig. 14. CPO combined with steam reforming.

reactor using our novel supported metal-alloy catalyst. Note that the product composition is essentially at equilibrium even with this extremely high space velocity. In Fig. 14, the “methane conversion” versus “time on stream” shows that this catalyst system is unusually stable; no initial deactivation period occurs, consistent with its non-coking behavior. A second but important benefit of this catalyst combination system is the closer approach to thermal neutrality, thus simplifying heat management and improving thermal efficiency.

4. Utilization of advanced tools

The development of new catalytic technology often requires effective deployment of a multi-disciplined team. In addition to using diverse skills, many advanced tools are employed, ranging from dynamic process simulators, to advanced control, and kinetic modeling. Computational fluid dynamics (CFD) is one of the advanced tools we frequently use in reaction engineering. One example is shown in Fig. 15, where the combustion products’ flow patterns are used to design new ethylene heaters. Here, the objectives are to optimize heat input distribution and to minimize NO_x emissions. In many situations, this effort can reduce or even eliminate the need for a selective catalytic reduction (“SCR”) unit downstream of the furnace. The left picture is a simulation in which the flow patterns are depicted by theoretical particle pathlines, and the right plot is the relative heat flux profile. Note that the model closely predicts the experimental results. We have used CFD in the development of many processes, including the AlkyClean process to control the local *iso*-butane to butylene ratio as a means to optimize product selectivity and catalyst stability.

Another advanced tool is high throughput screening (HTS). Many applications of this powerful technique have been previously described for catalyst testing, and Lummus



(a) (b)

Fig. 15. Furnace flow patterns (a) and heat flux profiles (b) in ethylene heaters.

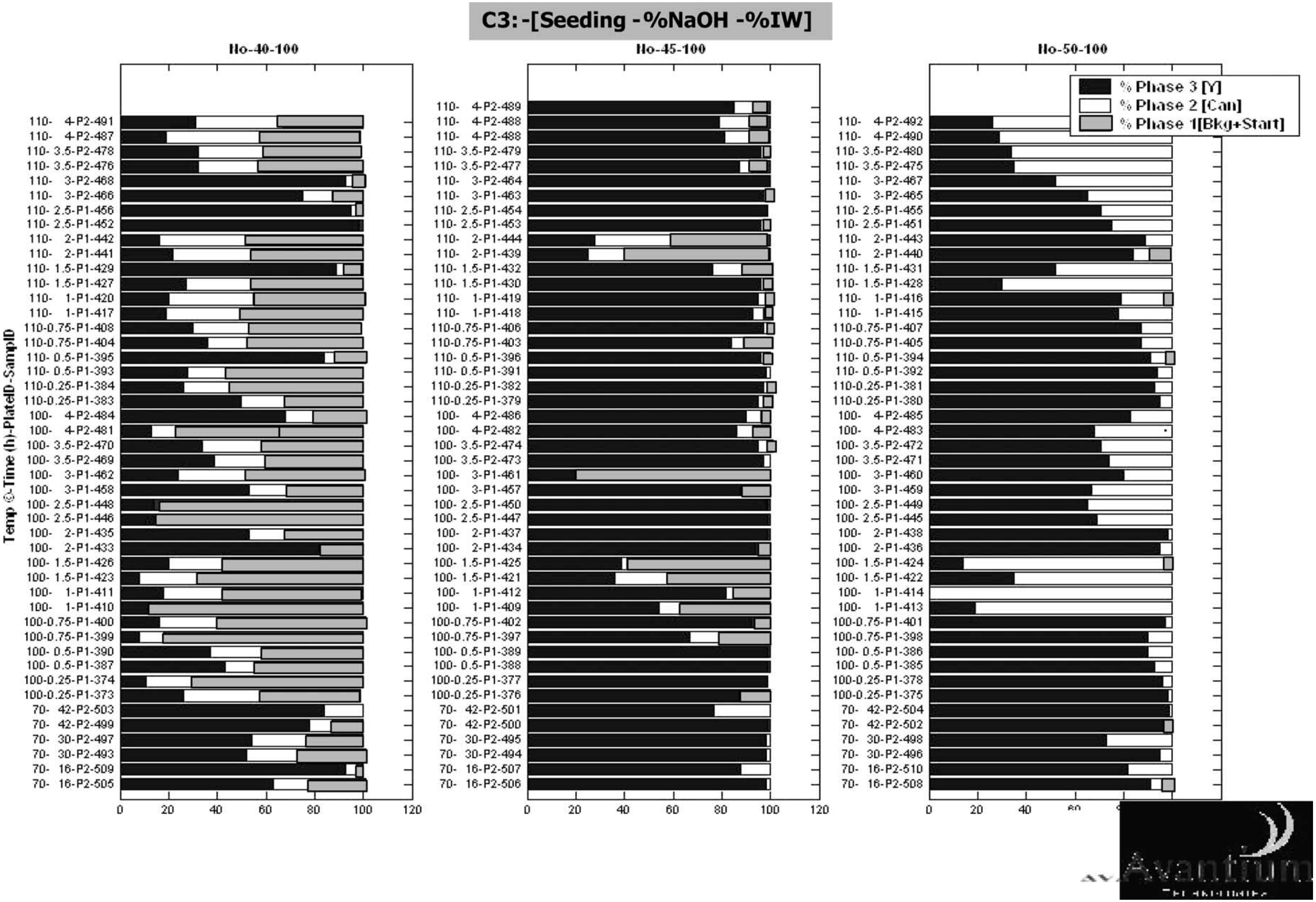


Fig. 16. Summary of HTS synthesis experiments.

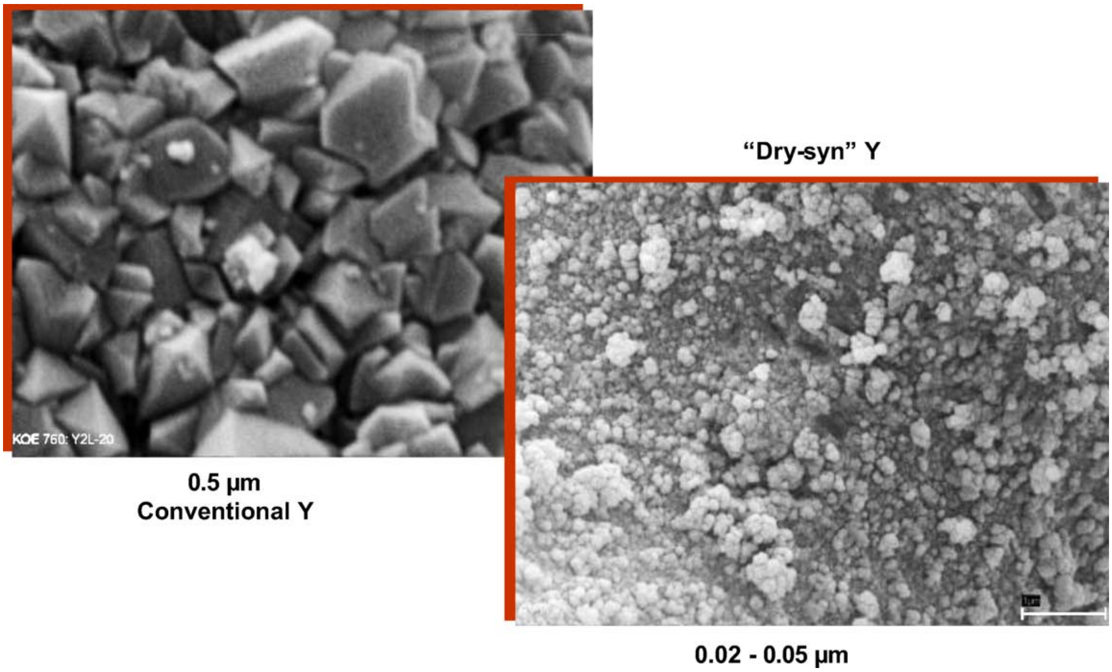


Fig. 17. Comparison of conventional and “Dry-Syn” Y crystallites.

has used this approach in catalysis in several areas. However, the example discussed here is quite different. Working with Avantium NV, we set out to devise a rapid screening method for zeolite synthesis. Our goal was to crystallize zeolite Y at the sub-micron scale—the region normally limited to templated zeolites such as ZSM-5 and zeolite Beta. In Fig. 16 we see a summary of many synthesis experiments where several parameters were varied [8]. Each bar represents one experiment. Shown are three major products: unconverted material (Phase 1), undesirable by-products such as cancrinite (Phase 2), and the targeted product, zeolite Y (Phase 3). Looking at this map one can quickly “zero in” on the experiments where zeolite Y is the predominant product. Of course, this is just the beginning of the analysis. After that, one must still measure percent crystallinity, surface area, hydrocarbon sorption capacity, and ultimate crystal size. Fig. 17 shows the dramatic success of this study. The left picture shows a typical zeolite Y crystal size of 0.5 micron, and the right picture shows our product of 0.02–0.05 micron. We believe that this zeolite Y’s crystal size is lower than any other reported in the literature. Since zeolite Y is the catalytic workhorse of the refining industry, one can immediately imagine its potential value in reactions that are limited by intraparticle mass transfer.

5. Industrial alliances

In order to accelerate process development and stimulate innovation, cooperative partnerships can be helpful, especially if each partner has different and complementary capabilities. Our previously described AlkyClean process project brought together ABB Lummus Global (a diverse engineering and technology company), Akzo Nobel (a world leader in catalyst manufacturing), and Fortum Oy (a Finnish refining company with a track record of embracing innovation and environmental responsibility). In addition, we have formed three technology joint ventures:

- CDTECH, with CR&L (a CRI International company)
- Chevron Lummus Global, with ChevronTexaco
- Novolen Technology Holdings, with Equistar.

The example described here will revolve around CDTECH, where catalytic distillation was developed. As the phrase implies, catalytic distillation (CD) [9] involves simultaneous reaction and product distillation. CD processes are particularly well suited for processes where the feed and product have a different boiling range, thereby facilitating separation and enhancing selectivity. The predominantly liquid phase facilitates heat management and aids catalyst life stability. The family of CD technologies is quite broad, and today the number of commercially licensed units is approaching 150.

Table 1 shows some of the CD applications that have been commercialized [10–12]. One major example is

Table 1
Commercial applications of catalytic distillation[a]

Etherification (MTBE, TAME and ETBE)
Aromatics alkylation (EB and cumne)
Benzene removal from reformate
Selective desulfurization
Various selective hydrogenations

[a] Demonstration plant of Tianjin, China Front-end CD*Hydro*® process for ethylene plants (2003).

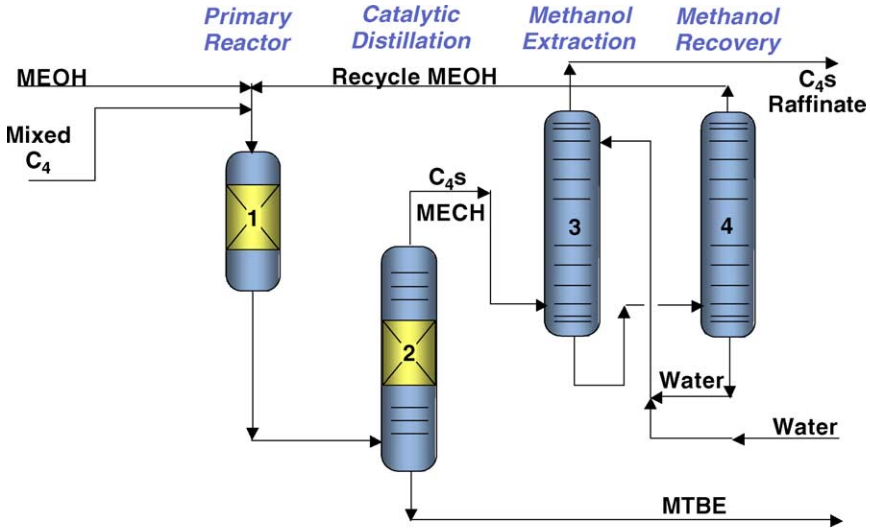


Fig. 18. Flow diagram of CDTECH MTBE (CD*Mtbe*$^{(r)}$) process.

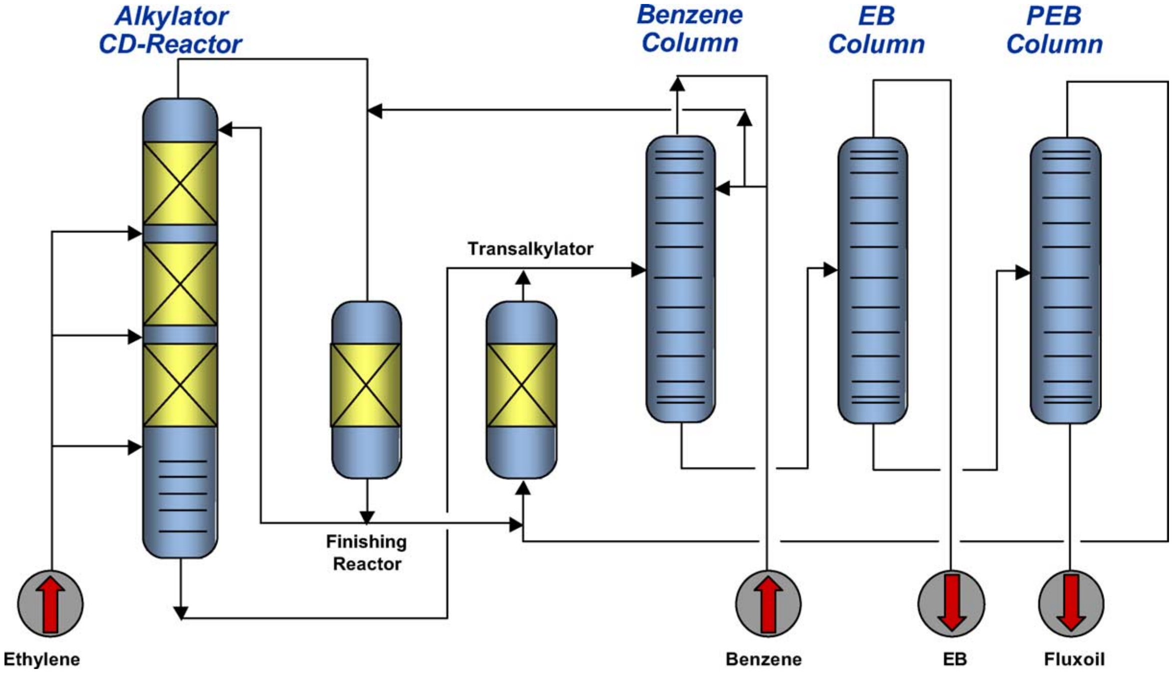
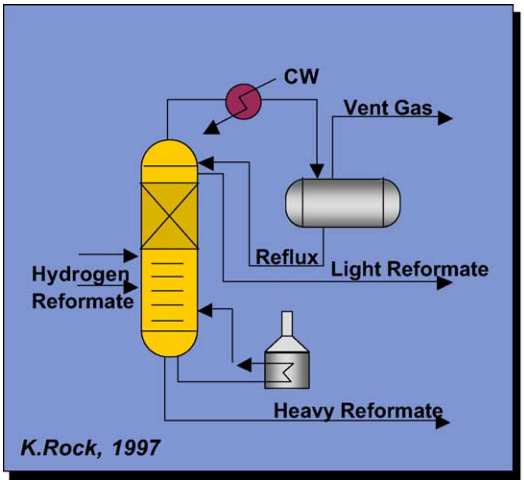


Fig. 19. Flow diagram of CDTECH *EB*® process.

etherification for oxygenates production (Fig. 18) shows the CD*Mtbe*® process). Another example is aromatics alkylation (such as EB and cumene production). Fig. 19 shows the schematic of the CDTECH *EB*® process. There are also several ultra-clean fuels processes. (Fig. 20 illustrates the CD*Benzene* process to selectively hydrogenate benzene, and Fig. 21 shows one of our many process configurations to remove sulfur from FCC gasoline.) One selective hydrogenation process—called "front-end CD*Hydro*®"—is shown in Fig. 22. While the ethylene process per se is "thermal," much of the product purification complex utilizes catalysis. Here, the term "front end" refers to the front end of the purification/separation system. The front-end CD*Hydro* process achieves two objectives simultaneously: (1)it consumes dilute hydrogen to eliminate undesirable acetylenes, thereby reducing refrigeration and compression costs; and (2) it combines reaction and separation in one step. This advance, integrated with several other Lummus innovations, created the most significant breakthrough in ethylene technology in the past 25 years.

6. Collaborations with universities and institutes

Industrial collaborations with universities and scientific institutes can stimulate innovations by opening avenues



- Low pressure operation
- Low capital cost
- Low hydrogen consumption
- **Selective benzene hydrogenation**

Fig. 20. New catalytic distillation technology—CD*Benzene*.

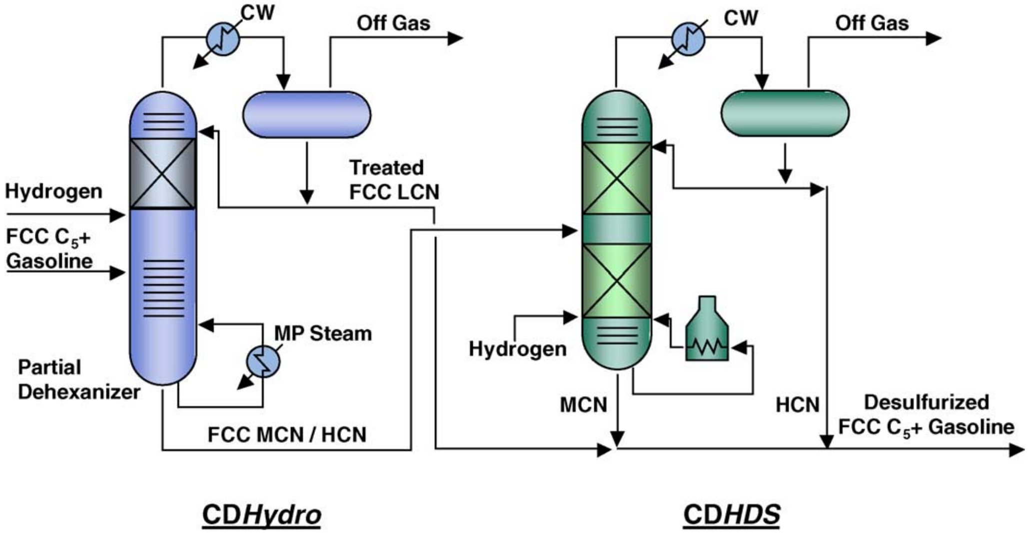


Fig. 21. FCC gasoline desulfurization via catalytic distillation.

for future technology developments. It can be a synergistic blend of new scientific concepts along with a "real-world" problem solving approach. While basic research at universities can be different in purpose and approach than applied industrial research, it is often quite similar in execution. Project collaboration can lower the transition gap from basic to applied research. Furthermore, talented students, not yet hindered by "conventional thinking," can be engaged in tackling difficult scientific challenges with creative approaches not yet employed. Of note, the university philosophy is to publish research results as soon as possible. This may lead to a conflict with the industrial partner, who wants to protect the intellectual know-how by patents and trade secrets. Our experience has shown that this issue can be managed if recognized and discussed at the project outset.

Some typical projects and the universities involved are listed in Table 2. Two examples will be described in more detail to illustrate how such projects can become the starting point for promising new technologies: (1) micellar catalysts and (2) mesoporous materials.

6.1. Micellar catalysts

Homogeneous catalysts often are orders-of-magnitude more active than heterogeneous catalysts, but suffer from

Table 2
Collaborations with universities—some typical projects

Massachusetts Institute of Technology (MIT) Cambridge, USA	Mixed oxides hydroisomerization catalyst
Technical University of Delft, Eindhoven, The Netherlands	Catalytic route to ethylene and propylene, Micellar catalyst
National University of Singapore, Singapore	Nano structured catalysts, Zeolite membranes, Methane upgrading
Washington University, St. Louis, USA	Reactor studies for alkylation, Hydrodynamics of structured catalysts

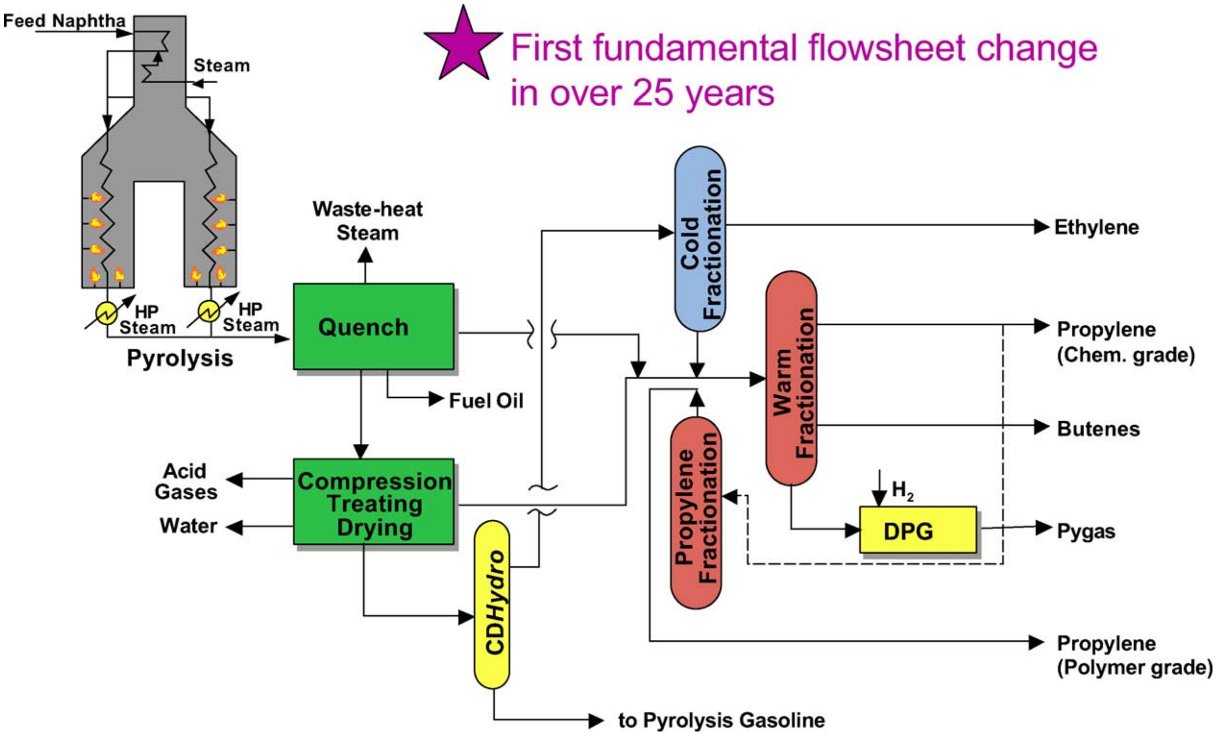


Fig. 22. Application of front-end CD*Hydro*(r) process in ethylene plants.

product/catalyst separation difficulties. As such, the anchoring of homogeneous catalysts has become an important research effort. One new technique of "heterogenizing" homogeneous catalysts involves encapsulating the catalyst in a porous, micellar structure made of surfactant molecules [13,14]. Several reactions have been investigated, including propylene oxidation using hydrogen peroxide as the oxidant [15] (Fig. 23). The results are very encouraging, showing that the reaction can occur at an appreciable rate with high selectivity at mild operating conditions. A conceptual process design (Fig. 24) based on these results indicates that the new technology may potentially become attractive due to its inherent simplicity [16]. By-product-free propylene oxide can be made at a considerably lower cost versus conventional technology. This is understandable since the complexity of the current propylene oxide/styrene monomer technology requires substantially higher capital investment. Further development of the new propylene oxide process seems to be warranted, especially if the micellar catalyst's structural stability can be made less prone to attack by hydrogen peroxide.

6.2. Mesoporous materials

Industrial and academic researchers have long sought to synthesize larger pore materials, i.e. larger than the pores of microporous zeolites. Conceptually, these "meso-porous" materials (i.e. with pores larger than 2 nm) should be useful for processing high molecular weight materials, such as petroleum residua, lubricants, amino acids, etc.

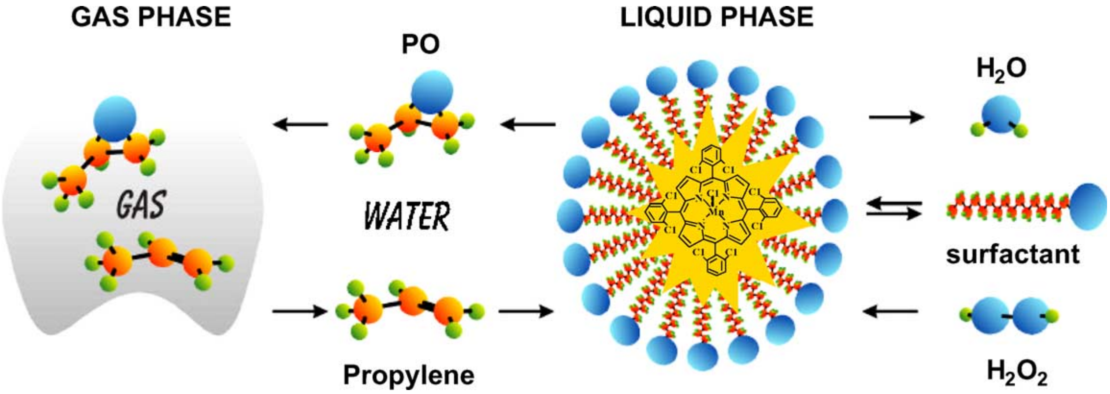


Fig. 23. Olefin epoxidation by a micelle-incorporated homogeneous catalyst.

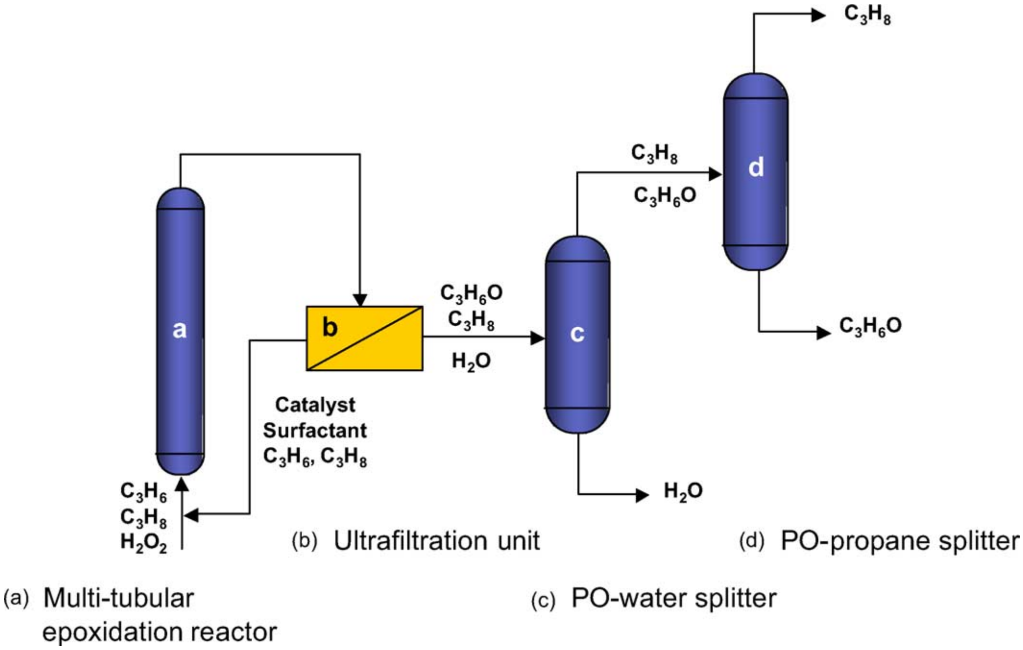


Fig. 24. Conceptual process flow diagram for propylene oxide.

Since discovery of the M41s family of crystalline mesoporous materials [17,18], an enormous worldwide effort has been expended on synthesis, characterization, and catalytic application. Unfortunately, these M41s materials generally lacked significant catalytic activity and also suffered from marginal structural, thermal, and hydrothermal stability. Many research programs sprung up to transform M41s into active and stable forms, but with mixed success. Many scientists then focused on other mesoporous materials, but so far no materials have shown to be both scientifically significant and relatively inexpensive to make.

In the late 1990s, Lummus established a joint research project with the Technical University of Delft (The Netherlands). The project's objective was to synthesize an

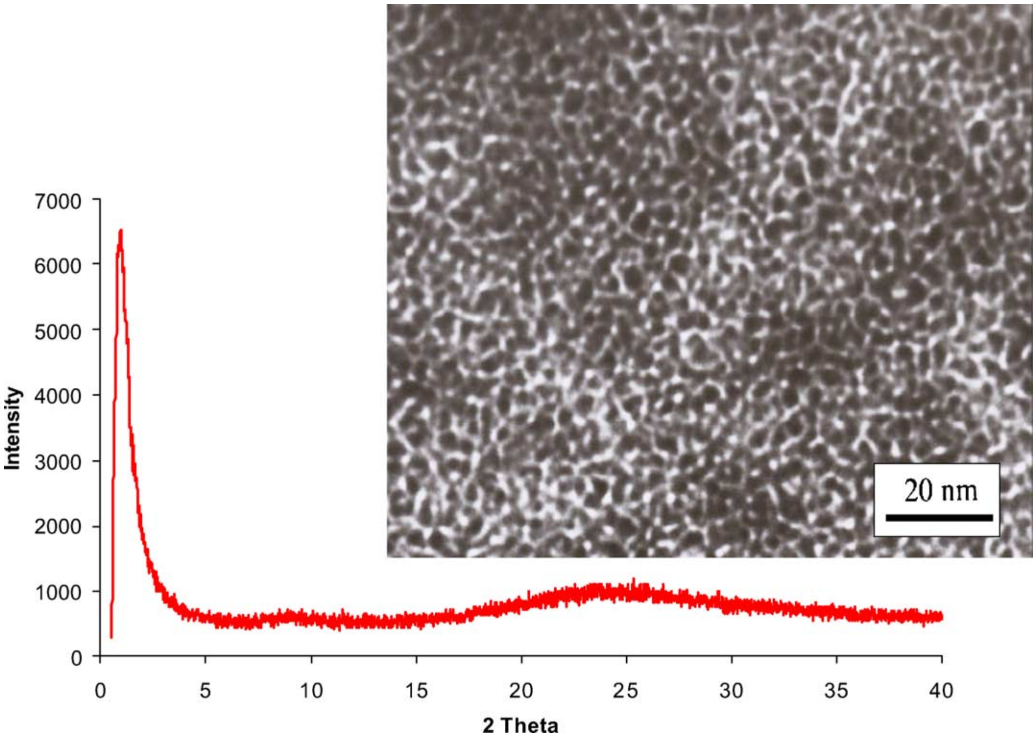


Fig. 25. XRD pattern and TEM of TUD-1.

industrially relevant, mesoporous material. The team discovered an entirely new family of mesoporous materials, now known as “TUD-1” [19–21]. Fig. 25 shows a typical X-ray diffraction pattern and TEM (transmission electron micrograph) of TUD-1. Using a novel characterization technique, TUD-1 has been shown to be an ultra-large pore, amorphous material having random, three-dimensional, interconnecting pores—very much like a molecular-scale version of a ceramic foam. Synthesis parameters can be varied to custom tailor the pore sizes and to make an extremely wide range of chemical variants (e.g. Si, Al, Ti, Cr, Sn, Ga, etc.) As a result, TUD-1 has been shown to be dramatically superior to other mesoporous materials. Compared to M41s, TUD-1 has significantly broader catalytic utility as well as enhanced structural, thermal, and hydrothermal stability. It has been shown to be an important catalyst for selective oxidation, acylation (for fine chemicals), hydrogenation, hydrotreating for ultra-clean fuels, and many other applications. While the conventional wisdom was that mesoporous materials’ primary utility would be for high molecular weight chemicals, TUD-1 can also be an effective catalyst for many fast reactions where mass-transfer limitations play an important role. We have also shown that zeolite/TUD-1 composites can have a totally unexpected, synergistic catalytic value. It is fair to say that we have just touched the “tip of the iceberg” in the TUD-1 catalysis story.

7. Conclusion

Based on the examples laid out in this paper, it is easy to see that many factors can come into play in fostering innovation in catalysis. Each of these drivers has its own, unique dimension. Taken together, they form a patchwork with many nuances and interplay. The derived synergies make them far more valuable together than merely the sum of the individual drivers. The end goal is to mold these drivers and reap the benefits of catalysis to create value for a better society.

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