PERSPECTIVES: CHEMICAL ENGINEERING

New Avenues in Ethylene Synthesis

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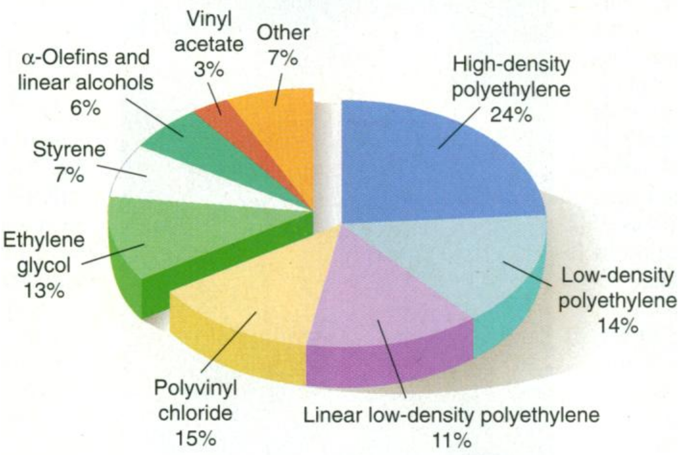
There is considerable economic incentive in the petroleum and chemical processing industries to transform cheap and abundantly available starting materials (feeds) into desirable, higher value fuels and chemicals. Such transformations are often achieved with the use of heterogeneous catalytic reactors. Over the past few decades, a number of different catalysts and reactor designs have been explored for the conversion of light hydrocarbons. One problem encountered in many of these systems is that higher feed conversions across the reactor lead to a decline in the selectivity to desirable products, thereby negatively impacting process economics.

Over the past few years, L. Schmidt and co-workers at the University of Minnesota have explored the feasibility of a particular type of reactor for the one-step synthesis of syngas (a mixture of carbon monoxide and hydrogen used in synthesis), alkenes, and oxygenated products at reasonably high conversion rates and selectivity. The reactor is a highly-porous, catalyzed foam monolith. The reactants flow through the foam at high velocity and are converted to products. At a reactor temperature of around 950°C, the residence time of reactants within the reactor is a millisecond or less. On page 712 of this issue (*1*), Bodke *et al.* report that, using such a reactor and a Pt-Sn catalyst, ethane can be converted to ethylene in yields exceeding that of an ethane steam cracker, a well-established commercial process. This result and the underlying technology could have considerable commercial impact. Ethylene is one of the largest volume chemical intermediates in the industry (see the figure), with growth driven by the polyethylene market (*2*).

As often, there is a question of whether the results are evolutionary or truly revolutionary. The authors have been studying alkane oxidation and oxidative dehydrogenation using similar catalysts and reactors for many years (*3*, *4*) and have previously demonstrated ethane oxidative dehydrogenation using Pt and Pt-Sn foam monoliths. However, the results in the present report are particularly noteworthy. Ethane conversion of as much as 70% is reported at 950°C for a 2/1/2 ethane/oxygen/hydrogen feed ratio and a residence time of only 10^{-3} s. The residence time is the ratio of the reactor volume to the volumetric flow rate, and therefore this reactor will be much smaller than an ethane cracker that has a residence time of around 1 s. The addition of substantial amounts of hydrogen to the ethane-air mixture over a Pt-Sn catalyst appears to increase ethane selectivity and to suppress carbon oxidation reactions. A high ethylene selectivity of 85% with low carbon oxide formation of 5% is claimed. More hydrogen is produced by the reactions than is fed to the reactor. Despite the 2/1 hydrogen-to-oxygen ratio in the feed, no flames or explosions are observed in the presence of ethane.

The authors convincingly argue that a purely homogeneous reaction mechanism cannot explain the observations. Only the Pt-Sn is capable of the observed high ethylene selectivity and low carbon oxide formation, and therefore surface chemistry and catalysis are likely to be very important. The fact that at high temperatures, the nonequilibrium product ethylene (rather than the thermodynamically favored carbon oxides) is almost exclusively formed is unexpected. It seems that hydrogen oxidation and ethane dehydrogenation occur in parallel with minimal chemical interaction between the reaction pathways.

Commodity plastics consume majority of U.S. ethylene



1998 consumption = 52 billion pounds (23.6 billion kg)

To better understand the overall process, the effect of the Pt-Sn catalyst has to be separated from transport phenomena predictable under operation conditions. To do so, an analysis of heat and mass transport processes in these reactors is warranted. Hydrogen oxidation is a facile exothermic reaction, whereas ethane dehydrogenation is endothermic. Hydrogen has a higher diffusivity than the other reactants. The nonlinear coupling of heat and mass transfer and kinetics can result in surface temperatures much higher than the gas temperature, perhaps even higher than the adiabatic temperature (*5*). Such conditions shift the dehydrogenation equilibrium in a favorable direction.

At operation temperatures, the reactor is glowing hot and both heterogeneous and homogeneous reactions are expected. Thus, in addition to traditional chemical reaction engineering considerations, the impact of radiation in maintaining temperature and temperature uniformity within the reactor and the role of heterogeneously assisted homogeneous reactions will have to be assessed. Such analyses will provide guidance on reactor geometry and scale up criteria for this new type of reactor.

The next step will be to move from the small-scale synthesis in the laboratory to larger scale synthesis in a pilot plant. As the project moves through piloting, questions regarding the stability of the active site and the monolithic support will undoubtedly be addressed. Sintering and perhaps volatilization of the noble metal ingredients will create a need for catalyst addition or replacement strategies. Local temperature gradients and fluctuations within the monolith support can cause thermal stresses that induce mechanical degradation and sintering. Some of these materials problems, although manageable on the laboratory scale, often manifest themselves on a larger scale and will have to be addressed.

An overriding issue in the scale-up will be process safety. As the authors discuss in their report, a 2/1 mixture of hydrogen and oxygen should be either flammable or ex-

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plosive. An improved understanding of the flammability and explosion limits for their ternary mixture at elevated temperature and in the presence of solids is needed. Given that the reactor operates at the edge of the reactor materials' durability envelope, mixing and control issues will be important.

Along with technical hurdles, business forces will inevitably determine the pace of commercialization. The reactor volume for the present process will be considerably lower than that of an ethane cracker; however, catalyst replacement and disposal costs will have to be factored into the economic analysis. A head-to-head analysis of carbon atom utilization and operating costs versus ethane cracking is needed. A key issue is whether the technology can be easily retrofitted into existing plants. Detailed characterization of products and pilot studies containing recycled streams should help answer these questions. For new plant constructions, an acceptable technical risk and financial hurdle rate will have to be defined.

The Bodke *et al.* report calls to attention several horizons for future research. The possibility of using similar chemistry for synthesis of other chemicals, especially in cases where endothermic and exothermic reactions are coupled, needs further exploration. To alleviate safety concerns, basic research on the explosion and flammability limits of gas mixtures with and without solids present is needed. The nature and morphology of the active catalytic site, surface kinetics, and the role of homogeneous reactions in determining product selectivity in these reactors will need to be better understood. Modeling tools containing heterogeneous and homogeneous kinetics will have to be extended to include mixtures of higher molecular weight hydrocarbons. From a materials standpoint, thermally stable supports and reactor design concepts may have to be developed. Despite the technical challenges, the chemistry, and the high temperature, short contact time reactor technology developed by Bodke *et al.* is likely to present opportunities for discovery and engineering in what is considered by some to be a mature industry.

References

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PERSPECTIVES: EARTHQUAKE GEOPHYSICS

Deep Slip Rates on the San Andreas Fault

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Parkfield, California, located along the San Andreas fault, is affectionately known to the local inhabitants and some Earth scientists as the "Earthquake Capital of the World," but to most people the town—with a population of 34, according to a sign at the outskirts—is hardly on the map. Because of an unusually regular sequence of magnitude (*M*) ~ 6 earthquakes since 1857 (*1*), the Parkfield segment of the San Andreas fault has been the subject of a focused earthquake prediction study since 1985. The approximately *M*6 earthquakes in the Parkfield sequence occurred on average every 22 years, with the last one in 1966. In 1985, the next event was thus forecast to occur in 1988 ± 5 years (*1*). Although the expected earthquake has still not occurred, the data have become a rich source of information about the behavior of this part of the San Andreas fault system, and the observations may have important implications for other areas of earthquake hazard where the population density far exceeds that at Parkfield.

A fascinating example of what such a data set can tell us about fault behavior is presented by Nadeau and McEvilly on page 718 of this issue (*2*). At Parkfield, an array of seismometers is installed in boreholes at ~250 m below the surface. Borehole seismometers have much higher sensitivity than surface instruments because they are remote from surface noise sources. The borehole seismometers are arrayed around the epicenter of the 1966 earthquake, close enough to the epicenter to locate earthquakes with magnitudes as low as about −1.

Over the past 11 years, most of the 6000 microearthquakes detected by the Parkfield seismometer array occurred in spatially distinct clusters. Most of the 300 clusters that have been recognized (*2*, *3*) have experienced a sequence of up to 20 repeating "characteristic" earthquakes. Each microearthquake is virtually identical to the others in the same sequence, not only in location but in seismic characteristics. It seems that at each cluster, the "same" earthquake occurs over and over again.

Even though both cluster and noncluster microseismicity occurs, over 99% of the area of the San Andreas fault plane slips without microearthquakes (*2*). It is not known why most of the surface area of the fault creeps quietly, whereas only certain very localized spots slip via microearthquakes, but my guess is that it results from differences in rock type. It has been shown (*4*) that frictional sliding of some rock types becomes harder as the slip velocity increases (velocity strengthening) and weaker for other rock types (velocity weakening). Elastically loaded velocity-strengthening materials slide stably, whereas velocity-weakening materials slide unstably (*5*). This explanation seems to fit the spatial distribution of microseismicity at Parkfield. To the southwest of the fault, the rocks are relatively homogeneous granites, whereas the Franciscan formation on the northeast side is much more heterogeneous (*6*). The Franciscan rocks east of the 1966 epicenter are a melange, with clumps of harder rock including sandstone, greenstone, and chert dispersed in softer mudstones. Laboratory data on similar materials suggest that these clumps are velocity weakening, whereas the mudstone is velocity strengthening (*4*). This would result in microearthquakes where the harder clumps rub the granite across the fault and in fault creep everywhere else. The suggestion is that every time enough stress has built up by slow slip between the surrounding mudstone and the granite, each small harder patch jerks forward in another microearthquake.

Regardless of the correct explanation for the clusters of repeating earthquakes, Nadeau and McEvilly (*2*) have put them to good use to determine the slip rate for the fault at depth as a function of space and time. Creepmeters across the fault show how it slips at Earth's surface, but slip at depth has to date only been inferred by indirect methods (*7*, *8*). The observations reported by Nadeau and McEvilly (*2*) are not as direct as would be obtained by a creepmeter installed across the fault at a depth of 10 km, but this would be a technically almost impossible task. The assumptions involved in their inferences of slip rate are simple and any errors introduced should not change the general interpretation. Each repeating earthquake has virtually the

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