Engineering Consulting & Training Services

CARMAGEN Engineering, Inc. eNewsReport

January 2012

Nano Refining

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The popular perception of a petroleum refinery generally conjures up images of large-scale towers, vessels, reactors, pumps, and compressors facilitating processes measured in thousands of barrels or tonnes of crude oil, steam, and derived products. What is less appreciated is how much of modern refining is pinioned on the use of materials whose functions can only be properly understood and controlled by delving into the world of the very small. That refineries operate today at a high efficiency, can largely be attributed in good part to a shift from property-based processing, reliant on bulk measures such as viscosity, boiling point, pour point and color, into refining strategies tuned to transformations at the molecular level enabled by new materials. Modern refining is the confluence of macro-scale engineering with nano-scale catalytic chemistry.

Petroleum refineries today use highly sophisticated process models to track and control hydrocarbon molecules through multiple steps, some of them mediated by catalytic materials designed with precisions below 10^{-10} meter. Zeolites are one such class of materials with microporous crystalline structures that have had a big impact on efficiency. They comprise atomic linkages of silicon-oxygen and aluminum-oxygen in tetrahedral arrangements to form anionic lattices having a regular structure. Another class of microporous crystalline solids known as SAPO's is based on anionic lattices formed from oxygen bound to silicon, aluminum, and phosphorus. In each case, when the counter-cation needed to form the neutral structure is hydrogen, zeolite and SAPO-based materials can facilitate a wide range of acid catalyzed reactions such as alkylation, cracking, hydrocracking, and hydroisomerization. It is the ability to finely control pore shape, pore size, and the chemistry inside and outside these pores that has made these materials far superior to earlier generations of catalysts based on amorphous aluminas and silica-aluminas with no regular structure.

The choice of zeolite for a given process depends on the task. Fluidized Catalytic Cracking (FCC), for example, is a process that converts gas oils and heavier oils into gasoline, jet fuel, and diesel by carbon-carbon bond cleavage. Modified Zeolite Y-type materials, synthetic variants on the mineral faujasite, can accomplish this with far more specificity than the amorphous alumina and silica-alumina based materials once used. Zeolite Y created a step change in materials design and capability when it replaced amorphous catalysts in FCC units in the 1960's. The interior surface geometry and charge intensity, derived from the field created by the anionic framework and the cationic hydrogen sites, generates a surface and environment not possible with amorphous materials. With continued fine tuning of structure and chemistry, zeolite based catalysts make FCC today a most efficient, reliable, refinery workhorse. The revolution

Work Highlights

Heavy Lift

- *Reviewed the lift plans developed by a refinery, their mechanical contractor, and crane contractor for replacement of the top head and cyclones of an FCCU Regenerator vessel. The review consisted of reviewing the lift plan itself, along with a civil engineering review of the crane foundation design and calculations, and mechanical engineering review of the vessel attachment designs and supporting calculations. Various recommendations were provided in each area, and the lift proceeded without incident.*

Process, Operations & Safety

- *Assisting a licensor with an FCC optimization study of an overseas refinery, with possible support later on the implementation of recommended design improvements.*
- *Supporting the development of an electronic safety module for a client's training program for process engineers.*

that began with Zeolite Y continues to this day with the introduction of new kinds of synthetic microporous materials across the petroleum refining (and chemicals processing) spectrum.

Zeolites and SAPO's can be broadly categorized by the size of their pores, indicated approximately by a "ring number" equal to the oxygen linkages needed to define the pore circumference, and the dimensionality of the pore system. Materials like Zeolite Y are "12 rings" and have pores in three dimensions. They have pores large enough to admit most of the hydrocarbon molecules in gas oils. Further, the large interior pore cavities are large enough for the bulky transition states to form without steric hindrance then break down into cracked, smaller hydrocarbons in the desired fuels boiling range. Products include a limited amount of coke that is, of course, the fuel that then drives the endothermic FCC process through its cycles of reaction and regeneration/reheating of the catalyst by air burning.

Another group of microporous systems that have had a major impact on refining efficiency are those with 10-rings. The most famous member of this group is ZSM-5. Catalysts based on ZSM-5 were the first to be widely used for "selective hydrocracking." Representations of Zeolite Y and ZSM-5 are shown in Figure 1 below. On wide ranging feedstocks, the smaller 10-ring systems permit only linear or near linear hydrocarbon species or chain fragments to enter the pores where the active catalytic sites are located. With most other species sterically hindered from entry, it became possible to conduct selective, non-equilibrium, processing of just the high melting point paraffinic wax component of a feedstock. This had not been possible with earlier generation catalysts which have surfaces open to all species including larger and generally more polar hydrocarbons typically present in refinery streams that compete strongly with waxes for adsorption sites and subsequent conversion. In short, earlier amorphous based catalysis led to equilibrium products based on the chemistry of all hydrocarbon species present, whereas ZSM-5 based catalysts imposed a shape criterion that skewed the process toward conversion of paraffins and near paraffins only.

Catalysts based on ZSM-5 were the first to be widely used to generate base oils and middle distillates having low pour points without using traditional, higher operating cost, solvent-based processing. ZSM-5 can be composited into catalysts that function for selective cracking or hydrocracking, converting wax into lower boiling components such as butanes and propane and their olefin equivalents. This outcome is governed by ZSM-5's unique pore geometry. It has a two dimensional network of pores that intersect and it is at these intersections where there is just sufficient space, by fractions of a nanometer, to allow the transition states to form that lead to cracked and hydrocracked products. At the same time there is very little room for other linkages to form and consequently little coke is generated. This is an important feature for a fixed bed process, which must function over long periods of time without need for reactivation or regeneration.

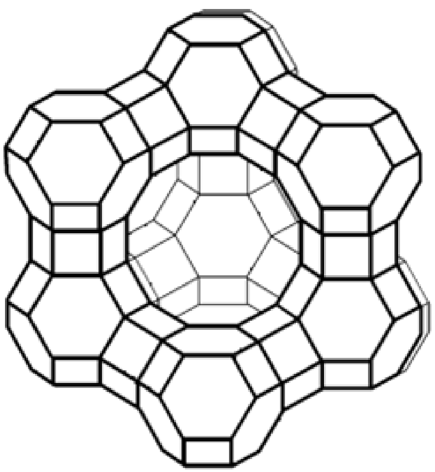
More recently, a further advance in the selective processing of waxes has occurred using other 10-ring zeolites that enables hydroisomerization of wax rather than hydrocracking. In this case, the wax component of a hydrocarbon feed stream, rather than being downgraded to fuel value as with ZSM-5 based catalysts, is converted with high efficiency into low melting point isoparaffins having a boiling range similar to the feed wax. Consequently yields of "dewaxed oil" in these processes are much higher and importantly, the isoparaffins generated from the wax have excellent properties. They provide features such as low volatility, low temperature fluidity and high viscosity index for Group II and III base oils for premium lubricants and high cetane number for top quality diesel fuels.

These improved microporous systems differ from ZSM-5 in having parallel pore channels without any intersection points such that there is no longer space for the relatively bulky intermediates to form. Consequently hydrocracked product formation is minimized, but there is just enough space for trigonal carbenium ions to form along the hydrocarbon chain. These species represent the transitional mid-point in the conversion from paraffin to isoparaffin through olefin intermediates. The catalysis here is bifunctional, requiring dehydrogenation then hydrogenation steps over a metal site (such as platinum) and acid catalysis via the hydrogen site in the micropores. Each one of these and other synthetic one dimensional 10-ring family are subtly different in pore dimension and pore shape (ellipticity). They can be further tuned by changes to the charge density location within the pores and amount, type and location of the metal sites. This can affect the branch size and spacing between branches along the paraffin backbone directly affecting the properties of the isoparaffinic oils.

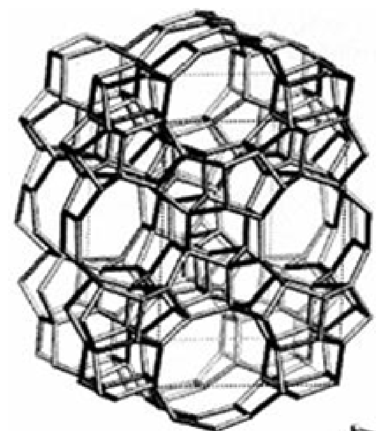
A large number of uniquely different materials now exist or can be made to address a specific objective for an increasingly wide range of refining processes. Fit-for-purpose microporous materials are being introduced into traditional processes such as alkylation, aromatization, and hydrofinishing. As well, opportunities now exist for processing in ways not possible with earlier generations of catalysts. The refinery of today may look unchanged from the outside, but on the inside is far more efficient at managing and converting hydrocarbon molecules.

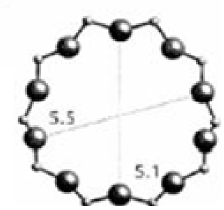
Thanks to these new materials, the nano-refining era has arrived, generating significant improvements in quality, yields, and energy conservation through more efficient processing.

Figure 1



Zeolite Y
a 12-ring zeolite
with 0.8 nm diameter pores





ZSM-5
A 10-ring zeolite
with 0.55 nm
diameter pores

About the Author

Ian Cody has over 30 years experience in lubes hydroprocessing, catalysis, and energy efficiency initiatives in refining. He worked as a Senior Scientific Advisor in the Fuels Process Research and Modeling Laboratory, ExxonMobil Process Research Laboratories in Clinton, New Jersey. Ian's creativity and leadership skills have contributed to building a vibrant Energy Reduction R&D activity in EMRE with several new technologies being identified in this exceedingly challenging area. He also served as Chairman of the organizing committee for the Longer Range Research Meeting from 2004 to 2008.

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