Zeolites as Catalysts in Refining

CHM 7100 project

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Crude Oil Refining

- Crude oil in and of itself is of little use and market value
- An oil refinery separates crude oil into various fractions based on differences in boiling point. This process takes place in a distillation tower.
- The tower may be 13 ft in diameter and 85 ft high
- Inside the tower are 16-28 trays that allow for “redistillation” of fractions resulting in more efficient separation
- Fractions are removed from the tower at various levels called side-draws and are referred to as “straight-run” products
- Conversion processes such as catalytic cracking change the size and structure of the “straight run” hydrocarbon molecules after their separation in the tower. (Speight, 1998)

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Sarnia area refineries

- Suncor Energy Products Inc.
- Shell Canada
- Imperial Oil Ltd.
- Suncor and Shell both refine about 72,000 barrels (11400 m^3) of crude per day, Imperial about 120,000 barrels (19000 m^3) per day

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Refinery Fractions

Fraction	Distillation Temperature (°C)	Carbon #
Gas	Below 20	C_1-C_4
Petroleum Ether	20-60	C_5-C_6
Light Naphtha	60-100	C_6-C_7
Natural Gasoline	40-205	C_5-C_{10}
Kerosine	175-325	C_{12}-C_{18}
Gas Oil	above 275	C_{12} & up
Lubricating Oil	Non-volatile liquids	
Asphalt & Coke	Non-volatile solids	

Morrison & Boyd, 1987

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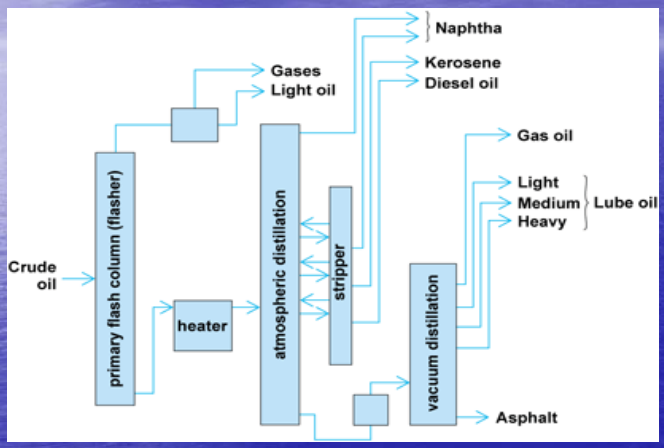
Distillation Section of a Refinery

"The Chemistry and technology of Petroleum", James G. Speight, 3rd Edition



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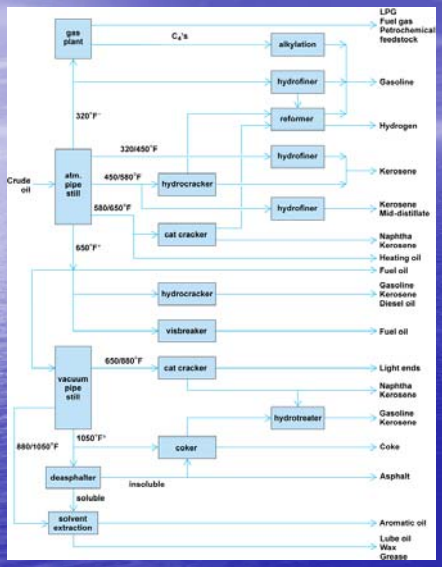

"The Chemistry and Technology of Petroleum", James G. Speight, 3rd edition, 1998, 748
A Refinery Schematic

A Petroleum Refinery Schematic

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Catalytic Cracking

- Catalytic Cracking was introduced to refining in the 30's in response to need for more gasoline and has superceded thermal cracking as it yields more of the desired high octane products
- It can virtually double the yield of gasoline type products from a barrel of crude oil
- Catalytic cracking is the process of breaking down the larger, heavier and more complex hydrocarbon molecules into simpler and lighter molecules to produce higher value products.
- It uses heat, pressure and a catalyst.
- (Speight, 1998)

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Catalytic Cracking con't

- In fixed-bed processes, the catalyst is in the form of small lumps or pellets in layers or beds in several (four or more) catalyst containing drums called converters
- Fluid bed catalytic processes are the most widely used and are characterized by the use of finely powdered catalyst that is moved through the processing unit
- Catalyst particles are of such a size that when aerated with air or hydrocarbon vapor, the catalyst behaves like a liquid and can be moved through pipes. Vaporized feedstock and fluidized catalyst flow together into a reaction chamber where the cracking reactions take place. (Speight, 1998)

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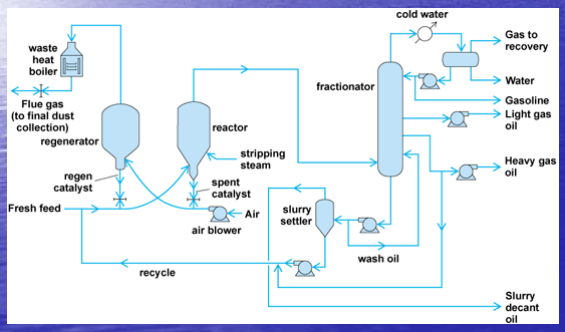
Fluid-bed Catalytic Cracking

- A fluid-bed catalytic cracking process diagram-"The Chemistry and Technology of Petroleum", 3rd edition,James G. Speight



Refinery Cat Cracker

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Hydrocracking

- Hydrocracking is similar to cat cracking with hydrogenation superimposed
- Produces either of the two major light fuels-high octane gasoline or aviation jet fuel
- "Hydrocracking achieves cracking with a rugged catalyst to withstand resid contaminants and a hydrogen atmosphere to minimize coking, a major problem in fluid catalytic cracking catalysts" (Riegel, 1983)
- Coke is a complex polynuclear material that is low in hydrogen. It can polymerize to graphite with very large aromatic sheets and no hydrogen. This graphitic material is both more thermodynamically stable and less kinetically reactive. (Speight, 1998)

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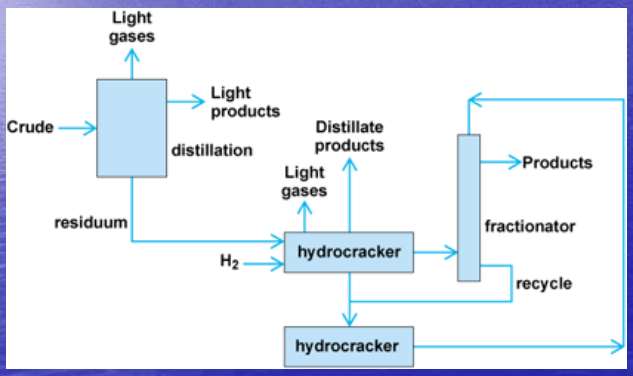
Two-stage Hydrocracking Process

- Two-stage operation maximizes yield of transportation fuels



"The Chemistry and Technology of Petroleum", 3rd Edition, James G. Speight

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Hydrocracking con't

- First stage is conversion of nitrogen compounds in the feed to ammonia by hydrogenation and mild hydrocracking. (Nitrogen containing compounds in the feed diminish cracking activity of hydrocracking catalysts.)
- Oil feed in second stage contain paraffins and aromatics boiling well above required gasoline or jet fuel product. Stage. Feed, now low in nitrogen compounds, is passed over second stage catalyst (zeolites). Conditions are 300-370 C, and 10-17 MPa hydrogen pressure. (Speight, 1998)
- Hydrocracking requires a dual-function catalyst with high cracking and hydrogenation activities. Typical levels are 25-50% weight zeolite in the catalyst with the remainder being the hydrogenation component-usually nickel, tungsten and molybdenum in the sulfide form. (Speight, 1998)

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Zeolite Catalysts

- Zeolite catalysts have been the primary catalyst type used in refining in the last two decades. Zeolite catalysts can operate in the presence of substantial concentration of ammonia in marked contrast to other silica-alumina catalysts.
- Zeolites are usually type Y (faujasite).
- Catalyst life of up to 7 years has been obtained commercially in processing heavy gas oils. Zeolites have up to 10,000 times the activity of so-called conventional catalysts in specific cracking tests.
- In the monomolecular mechanism, an alkane (paraffin) is protonated by a Bronsted acid site to form a five-coordinated carbon atom. The carbonium ion may undergo cracking to yield an alkane and an alkene, regenerating the acid site or it may dehydrogenate to yield H_2 and an alkoxide species. Desorption of the alkoxide yeilds an olefin and regenerates the acid site.

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- "Reactants are physisorbed in the pores of the zeolites (dominant interactions are the van der Waals interaction) and at high temperature are activated through proton transfer from the Bronsted acid sites. Because the rate-limiting step of monomolecular cracking is the protonation of the alkane, this reaction is an acid-base reaction between the zeolite and the alkane. Therefore, its intrinsic rate is a measure of zeolitic acidity." (B. Zu et al.2006)
- "The better the fit between pore and reactant, the higher the observed rate per Bronsted acid site of the reaction." (BXu et al.,2006)
- Crystalline structure of zeolites provide higher activities and controlled selectivity compared to amorphous silica-aluminas.

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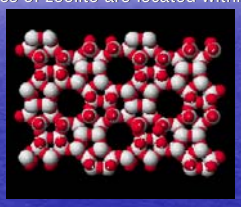
Catalysis using zeolites

- Combines properties of excellent thermal stability (>800° C), pore size of molecular dimensions
- Almost all reactive surface area and attendant acid sites of zeolite are located within the internal pore structure (>99%)
- Catalytic chemistries occur within the pores.



- A gram of zeolite has a surface area of 900 m^2 (Oliver, 2000)
- High concentration of active acid sites, their high thermal stability, and high size selectivity make zeolites the catalyst of choice in refining operations
- Limits the outcome of the chemistry to those products that can either fit into available space or migrate from the site of their formation to the exterior of the zeolite
- More than 90% of cat cracking catalysts in the US are zeolite based (Oliver, 2000)
- Zeolites are environmentally safe

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The Zeolite Structure

- Zeolites, from Greek, *Zein* "to boil", and *lithos*" a stone"
- The term zeolite was originally coined in the 18th century by Swedish mineralogist A.F. Cronstedt, who observed that upon heating the stone began to "dance about". This was due to the water adsorbed inside the zeolite's pores being driven off.
- Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves" i.e. they have the ability to selectively sort molecules based primarily on a size exclusion process due to a very regular pore structure of molecular dimensions
- Crystals are highly porous and are veined with submicroscopic channels

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Zeolite Structure con't

- Structure consists of a framework of tetrahedra usually with a Si or Al atom at the center. O atoms are at the vertices of each tetrahedron. "Vertex O atoms are each shared by two tetrahedrons so that every Si or Al atom within the tetrahedral cage is bound to four neighboring caged atoms through an O atom. Number of Al atoms in a unit cell is always smaller than, or at most equal to number of Si atoms because two Al atoms never the share the same O." (p 631. Speight)
- Important feature are loops of 4,5,6,8 and 12 membered tetrahedral rings which further link for four channels and cages (Moore)
- There are 192 Si and Al atoms per unit cell (Speight)
- Each unit cell contains eight sodalite (truncated octahedron) and eight α cages (Journal of Chem Ed Vol 79 April, 2002)

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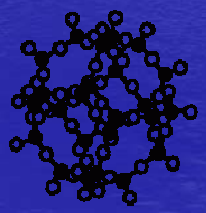
Zeolite structure con't

- "The volume per framework O atom is a measure of packing efficiency of the structure and zeolites have very high values, usually greater than 2.5 nm^3 per O atom" Zeolite" (Moore)
- Faujasite is a 12 membered ring and channel diameter of 0.9 nm permits passage of benzene rings (Moore)
- Zeolite faujasite (preferred form in catalysis) crystallizes with the composition $SiO_2(NaAlO_2)_x(H_2O)_y$ where x=1-10

www.gsaresources.com



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Zeolite Structure

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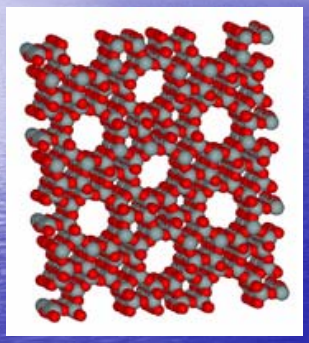

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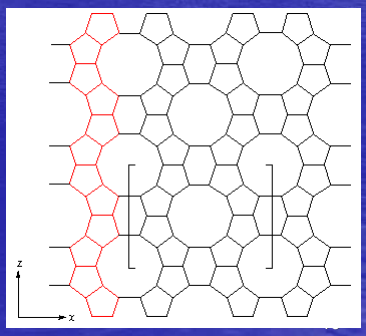

Zeolite Occurrence

- Usually white but may be coloured pink, brown, red, yellow or green by inclusion
- Low temperature, low pressure minerals
- Open framework structure lead to moderate hardness (3-5) and specific gravity low (2.0-2.5)
- Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins.

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Synthesis of Zeolites

- Zeolites can be synthesized hydrothermally starting from slow crystallization of a silica-alumina gel in alkaline environment using organic templates.
- Synthesized from solutions of sodium aluminate, sodium silicate and sodium hydroxide mimicking conditions found in the earth's crust where zeolites are formed naturally
- Particularly important to synthesis is the templating ion, usually propylammonium ion. Aluminosilicate lattice forms around this templating organic ion.
- Tunnel size is determined by the templating cation
- Other conditions such as temperature and pH determine precise zeolite formed

- Synthesis temperature is 450-100 with open framework structure occurring at the lower temperatures.
- Synthetic zeolites hold some key advantages over their natural analogs, including more uniform, phase-pure state. In addition synthesis allows for the ability to manufacture desirable zeolite structures which do not appear in nature.

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Effect of Metal Modifications of Y Zeolites on Sulfur Reduction

- Pang et al. have studied modification of zeolite to achieve a suitable acidity to effectively remove sulfur in refining operations

- Sulfur removal is increasingly necessary with stringent regulations to gasoline for meeting ultralow sufur levels

- Their studies found that modification of Y zeolite with Zn, V, Cu and RE could increase the total acidity of the zeolite

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