CATALYTIC CRACKING

One of the most important applications for Rare Earths is in the catalysts used for oil refining in processes known as Fluid Catalytic Cracking (FCC) and Alkylation. The catalysts primarily consist of man-made zeolite (alumino silicate) to which Lanthanum is added to stabilise the zeolite structure and improve catalytic activity.

FCC units are an essential operation in oil refining to convert heavy, high boiling point fractions of crude oil into lighter more valuable gasoline fractions.

FCC units improve the efficiency of oil refineries by up to 10% through higher gasoline yields and more efficient use of refinery feed stocks.

Crude Oil Refining and Zeolites

Crude oil consists of hydrocarbons with a range of molecule lengths and boiling points. This includes short chain, low boiling point / volatile gas such as propane through to long chain, heavy / high boiling point fractions such as bitumen. The most valuable components of crude oil are the mid-range hydrocarbons which are used for gasoline and diesel. The term cracking refers to the breaking of the long chain hydrocarbon molecule into shorter fractions. The selectivity of the catalyst to produce molecules in the gasoline range is an important characteristic.

Catalytic cracking was first employed in the 1940s to increase aviation fuel production and utilised natural clay minerals that contained aluminosilicate minerals that promoted the cracking of crude oil.

Zeolites are alumina silicates with specific structures and it was the development of Synthetic (man-made) zeolites with unique structures and high selectivity for gasoline that revolutionised oil refining in the 1960s.

The active constituent of an FCC catalyst is the zeolite which is an alumino silicate consisting of Aluminium, Silicon and Oxygen atoms arranged in regular structures that form a porous framework of “cages” and “super cages”. The caged structures vary according to the ratio of silica to alumina and the presence of other elements. A number of structures are depicted below of which two are particularly relevant to FCC for crude oil refining; type Y and ZSM-5.

Lanthanum in the Zeolite Catalyst

The raw zeolite is not very stable at conditions experienced in the cracking unit and without treatment the catalyst will break down and lose catalytic effect. The stability is improved by the addition of Lanthanum up to 3% by weight. The rare earth atom has a slightly smaller size and fits neatly within the “cages” of the zeolite where it acts to stabilise the zeolite structure.

Type Y Zeolite is the base type used for FCC. Structure consists of cages and super cages.

Type ZSM-5 Zeolite used for cracking of heavier crude oil and refinery residues. Rod type structure.
The FCC catalysts are produced by taking a zeolite and exchanging sodium ions located within the structure with ammonium and Lanthanum ions. After this ion exchange process the zeolite is washed and calcined at (500-600 deg C). At the high temperature the La ions migrate to positions inside the zeolite cages.

The solid catalyst material is separated from the hydrocarbon gases in a chamber employing cyclones. The “spent” catalyst is directed to a regeneration unit where coke is burnt from the surface and the catalyst is pre-heated ready for return to the mixing chamber.

It is in the regeneration step that Aluminium can be removed from the zeolite structure by contact with steam, which reduces the catalyst activity and weakens the physical structure of the zeolite. Lanthanum works to prevent this degradation of the catalyst.

The future of Crude Oil refining faces a number of challenges which call for new and improved catalysts that operate under different conditions and promote different reactions:

• Gasoline demand has flattened in the US and there is greater demand projected for diesel (Johnson), requiring catalysts that are more selective for diesel.
• There is a trend towards heavier feedstocks, and also lighter feedstocks, requiring more specific catalytic selectivity.
• Cracking of residue (heavy) fractions is important for refinery efficiency. The development of catalysts that can perform with the heavy fractions and selectively produce the desired hydrocarbon types is the primary area of R&D for the industry. The heavier hydrocarbons potentially block the porous structure of the zeolite, and are more prone to form coke on the surface of the zeolite. The residues also contain metals such as Nickel and Vanadium which occupy sites on the zeolite and “poison” the catalyst.

Lanthanum is a key component of Fluid Catalytic Catalysts and fundamental to the stability of the zeolite structures of the catalyst, and the selectivity of the catalyst for specific reactions.

Fluid Catalytic Catalysts are essential to the efficiency of oil refineries and this application will continue to be an important market for Lanthanum.

Information Sources


Weitkamp, J. Zeolites and Catalysis, Solid State Ionics, Volume 131, Issues 1–2, 1 June 2000, Pages 175–188