

Chapter 13

Role of Rare Earths as Catalysts in the Chemical, Petroleum and Transportation Industries



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13.1 Introduction

Rare earth elements, also known as the lanthanide series in the periodic table of elements, are a series of chemical elements found in the Earth's crust that are applied in many modern technologies such as consumer electronics, computers and networks, communications, clean energy, advanced transportation, health care, environmental mitigation, national defense and many others [1–5]. The introduction of the Welsbach incandescent lamp, which made use of the oxides of zirconium (Zr), lanthanum (La) and yttrium (Y) during the 1880s, marked the first commercial application of rare earths [1]. Since then, rare earths have found applications in various fields and their consumption has grown to over 100,000 metric tons annually as shown in Table 13.1.

Rare earths form a critical and essential part of many modern technologies as they sometimes act like technology building blocks. This is because their application in alloys and compounds can have a profound effect on the performance of complex engineered systems, some of which include automotive catalytic converters, petroleum refining catalysts, glass manufacture and polishing, ceramics, permanent magnets, metallurgical additives and alloys and rare earth phosphors for lighting, television, computer monitors, radar and X-ray intensifying film [1, 2, 6–8].

The demand for rare earth elements is a direct result of their integration as catalysts into end-use products. Catalysts represent a large market for rare earths where they provide properties desired for effective catalysis in petroleum refining, fuel additives and the transportation and chemical industry [1, 9–11].

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Table 13.1 Rare Earth Consumption by Market Sector [1]

Rare earth oxide	Amount by Market Sector (metric tons)								
	Catalyst	Ceramics	Glass	Metallurgy	Magnets	Battery alloys	Phosphors	Other	Total
CEO ₂	8820	840	18,620	5980		4040	990	2930	42,220
Dy ₂ O ₃	–	–	–	–	1310	–	–	–	1310
Eu ₂ O ₃	–	–	–	–	–	–	441	–	441
Gd ₂ O ₃	–	–	–	–	525	–	162	75	762
La ₂ O ₃	18,180	1190	8050	2990	–	6050	765	1430	38,655
Nd ₂ O ₃	228	840	360	1900	18,200	1210	–	1130	23,868
Pr ₆ O ₇	152	420	694	633	6140	399	–	300	8738
SmO	–	–	–	–	–	399	–	150	549
Tb ₆ O ₇	–	–	–	–	53	–	414	–	467
Y ₂ O ₃	–	3710	240	–	–	–	6230	1430	11,610
Other			480						480
Total	27,380	7000	28,444	11,503	26,228	12,098	9002	7445	129,100

13.2 Application of Rare Earths in Fluid Catalytic Cracking Catalysts

Fluid catalytic cracking (FCC) is a process for conversion of heavy oil fractions into high octane gasoline, light fuel oils and olefin-rich light gases. The process employs a catalyst in the form of microspheres, which behave as a fluid when aerated. Fluid catalytic cracking is an endothermic process during which carbon is deposited onto the catalyst. This carbon, known as coke, reduces the activity of the catalyst and the catalyst must be regenerated.

The fluidized catalyst is continuously circulated from a reaction zone, where the cracking reactions occur, to a regeneration zone where the catalyst is reactivated as illustrated in Fig. 13.1 [12].

During the FCC process, hydrocarbon (HC) feed is injected into the riser section of the FCC reactor where it is cracked into lighter more valuable products upon contacting hot catalyst from the catalyst regenerator. The catalyst and HC vapors are carried up the riser to the disengagement section of the FCC reactor where they are separated. Subsequently, the catalyst flows into a stripping section where the HC vapors entrained with the catalyst are stripped by steam injection. Following the stripping of HCs from the spent cracking catalyst, the stripped catalyst is recirculated to the catalyst regenerator.

Typically, catalyst is regenerated by introducing air into the regenerator and burning off the coke to restore catalyst activity. Coke combustion is an exothermic reaction and it is used to supply heat to the regenerated catalyst. The hot, reactivated catalyst flows through the regenerated catalyst standpipe back to the riser to complete the catalyst cycle. The coke combustion exhaust gas stream rises to the top of the regenerator and leaves the regenerator as flue gas. Flue gas generally contains

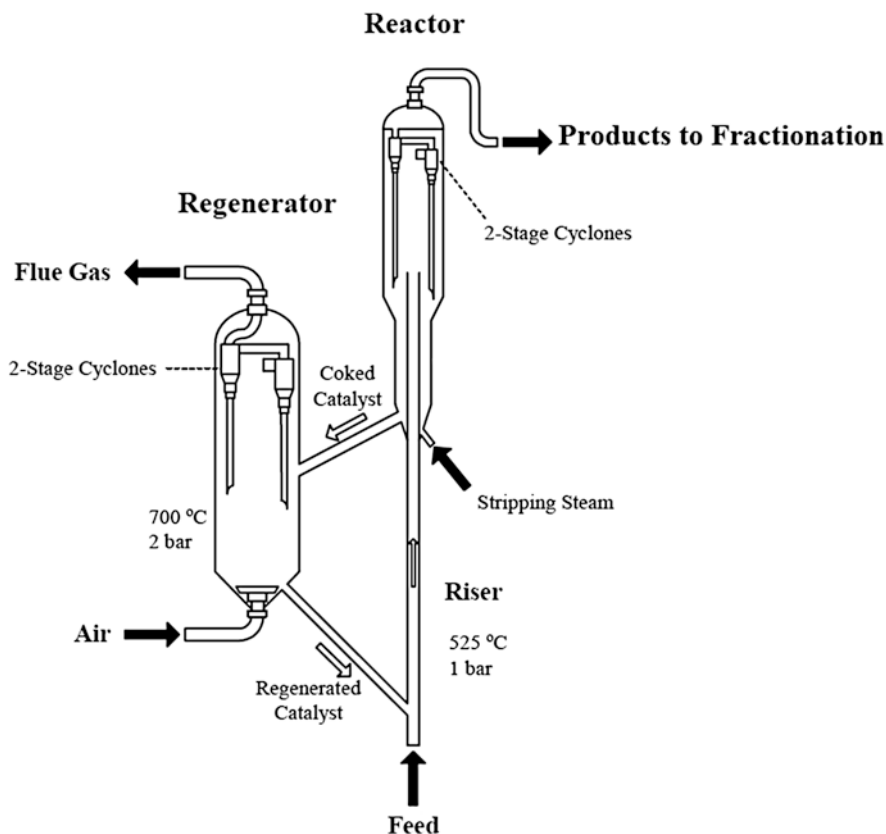


Fig. 13.1 Schematic of a conventional FCC unit [12]

nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), oxygen (O_2), hydrogen cyanide (HCN) or ammonia (NH_3), nitrogen (N_2) and carbon dioxide (CO_2).

In addition to providing the catalytic action, the catalyst is also the vehicle for the transfer of heat from the regeneration to the reaction zone. Catalyst performance is an integral part of the techno-economic evaluation of the catalytic cracking process as it affects the capital cost in terms of the amount of material required, and the quantity and quality of the reaction products generated.

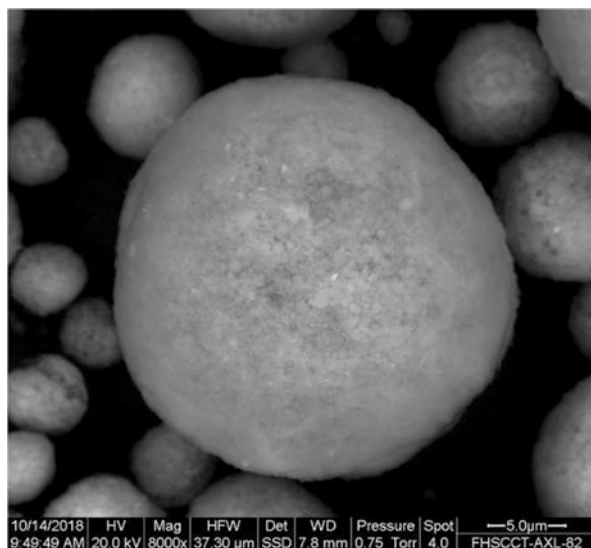
Rare earth oxides have been widely investigated in catalysis as structural and electronic promoters to improve the activity, selectivity and thermal stability of catalysts [1, 2, 10, 13–31]. Since the introduction of rare earths in fluid catalytic cracking (FCC) catalysts in the early 1960s, the FCC continues to play a major role in the catalytic application of rare earths [9]. The use of rare earths can help preserve catalyst effectiveness and increase the yield of the gasoline fractions by cracking the heavier oil fractions. Rare earths, such as lanthanum (La), are used in FCC catalysts to refine crude oil into gasoline, distillates, lighter oil products and other fuels.

FCC catalysts operate between moderate to high temperatures (500–800 °C) in the presence of steam, especially during the regeneration step. These severe conditions strongly influence the performance of the catalysts. Thus, thermal and hydrothermal stability of zeolites (i.e., hydrated aluminosilicate minerals, $M_xAl_xSi_{1-x}O_2 \cdot yH_2O$ where M is either a metal ion or H^+) are among the most important parameters for FCC heterogeneous catalysts.

One of the factors that affects the design and operation of an FCC unit is the type of catalyst to be employed in the process. Most FCC catalysts consist of an active component (e.g., zeolite), a matrix such as amorphous silica-alumina ($SiO_2-Al_2O_3$) which also provides catalytic sites and larger pores, a binder (e.g., bentonite clay ($Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)4O_{10}(OH)_2 \cdot nH_2O$)), and a filler. Fig. 13.2 is a micrograph of an FCC catalyst showing the spherical particles that are suitable for application in a fluidized circulating reactor. Large voids and pores in the spherical catalyst particle are necessary to allow for mass transport of the heavy HCs.

Ultra-stabilized zeolite Y ($M_{3.5}[Al_7Si_{17}O_{48}] \cdot 32H_2O$, M = Ca, Na_2 , K_2 , Mg) is used as the main active zeolite in today's conventional FCC process. This material contains an internal porous structure in which acid sites are present, which can convert larger molecules to the desired gasoline range molecules. Although the FCC unit was developed purposely to assist in the conversion of low value feed into more gasoline, the unit and the process have undergone several modifications, some of which are aimed at tackling the increasing demand for some of its by-products, such as propylene. For the purpose of producing more propylene and olefins, ZSM-5 (i.e., Zeolite Socony Mobil-5: $Na_nAl_nSi_{96-n}O_{192} \cdot 16H_2O$) is being used as the main active component of the catalyst in the FCC unit [35–42]. Metal contaminants usually have their biggest influence on the zeolite active components, and it is through the zeolite that rare earths are usually introduced into the FCC catalysts.

Fig. 13.2 Microscopic image of an FCC catalyst



The matrix of an FCC catalyst serves both physical and catalytic functions [32, 43–49]. Physical functions include providing particle integrity and attrition resistance, acting as a heat transfer medium, and providing a porous structure to allow diffusion of HCs into and out of the catalyst microspheres [20, 41–43, 45, 47, 48]. The matrix can also affect catalyst selectivity, product quality and resistance to poisons. Various alumina (Al_2O_3) and silica (SiO_2) sources are used to produce a meso- and macroporous matrix that allows access to, and pre-cracks the larger molecules in the heavy oil or crude oil. In addition, these components are used to bind the system together. Additional components may comprise rare earth metals or specific metal traps for trapping nickel (Ni) and vanadium (V) that are present in the feed source. The components are typically mixed in an aqueous slurry, and then spray-dried to form more or less uniform spherical particles that can be fluidized in a regenerator.

For the modern conventional FCC process, the desired catalyst properties are as follows: [33]

- Good stability to high temperature and to steam. The catalysts must have the thermal stability to maintain particle and catalytic integrity under severe regeneration conditions. The continuous cycle of cracking and regeneration in the FCC leads to dealumination as a result of the harsh hydrothermal conditions in the regenerator, and metal deposition from the feed. Dealumination leads to the loss of Bronsted acidity, while metal deposition can lead to occluded pores and unwanted secondary reactions. Kalirai [34] studied dealumination in FCC catalysts using scanning transmission X-ray microscopy (STXM) with La as a localization marker for the zeolite particles. Results revealed that the loss of activity in FCC catalysts is a combination of deposited metal-mediated pore accessibility loss and zeolite dealumination. Fig. 13.3 elucidates physical changes that occur within zeolite in the catalyst as a result of metal deposition and dealumination [34]. The thin ring of iron (Fe) deposition on ECAT 1 and ECAT2 (i.e., equilibrium

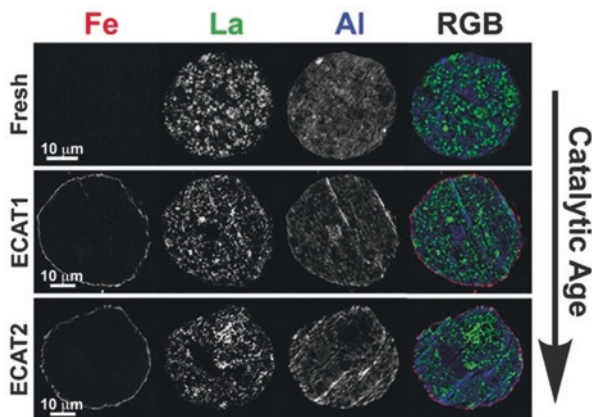


Fig. 13.3 Elucidation of zeolite dealumination using fresh and equilibrium FCC catalyst (ECAT) [34]

catalysts) is a result of the catalyst being exposed to feeds that contain contaminant metals (e.g., Fe). The deposited contaminant metals are primarily present on the surface of the catalyst.

- High activity to carry out conversion of the feed before any significant amount of thermal cracking sets in. Thermal cracking leads to undesirable products such as methane (CH_4), ethane (C_2H_6) and some propane (C_3H_8). Catalytic cracking produces relatively fewer C_1 and C_2 fragments and a larger number of olefins (C_nH_{2n}) are produced.
- Large pore sizes to crack larger molecules so that can get into smaller pores.
- Good resistance to attrition to maintain particle morphology under the severe impact and erosion forces that exist in the FCC unit.
- Low coke production so the catalyst can remain active for a longer period.

The main goal of the FCC unit is to upgrade low value HCs such as residue feeds, which often contains higher levels of contaminants that can degrade catalyst activity such as nickel (Ni), vanadium (V), sodium (Na), iron (Fe), and calcium (Ca) [32, 50, 51]. Of all these metals, V presents the most deleterious effect as it is mobile and can move from one catalyst particle to another, thereby contaminating newer active sites and aged catalysts. Figure 13.4 illustrates the distribution of Ni and V in the FCC catalyst before and after regeneration. It shows that Ni remains on the surface of the zeolite, while V is more mobile and penetrates into the pores of the zeolite. The mobility of V is facilitated during the regeneration process by the hydrothermal environment that is produced during the combustion of coke and HCs to steam and CO_2 .

The concentration of V in the spent catalyst is sometimes used as a determinant for the amount of fresh catalyst that is needed to be added to the FCC to maintain catalytic activity [24]. Vanadium also promotes dehydrogenation reactions leading to more dry gas and coke [52–56]. It also attacks the zeolite crystalline structure leading to structure collapse and a loss in surface area as the pore structure is no longer maintained.

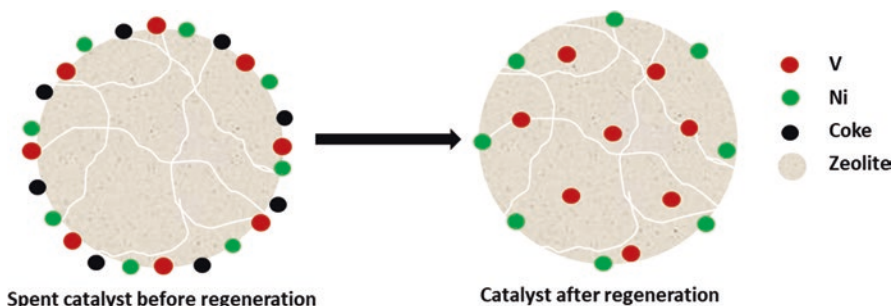


Fig. 13.4 Distribution of Ni and V in equilibrium FCC catalyst

13.2.1 Use of Rare Earths to Passivate Metal Contaminants

As described in the previous section, a common practice for maintaining the FCC unit activity is by adjusting fresh catalyst addition, based on the level of metal contaminants in the feed [57]. Fresh catalyst additions are increased when feed metals begin to increase, and the opposite applies when the metal content in the feed is low. Consequently, when dealing with feeds that have a higher metals content, adding more fresh catalyst alone may not be an effective catalyst management strategy as this will not reduce the impact of contaminant metals and the activity and stability of the catalyst will be adversely affected.

It is therefore important to have an appropriate catalyst formulation, which can effectively trap metal contaminants. The metal trap technology works by capturing the volatile and mobile metal contaminants, primarily V, to form a stable and catalytically inactive compound in a process known as *metal passivation*. Rare earths are used to passivate (trap) V through the formation of stable vanadates, thus preventing V from attacking the zeolite structure. The severe conditions under which the catalytic cracking process is carried out make it particularly difficult for V blocking. A suitable V trap for FCC catalysts should fulfill most of the following conditions: [58]

- The substance should be stable at a temperature up to 800 °C in an oxidizing environment (i.e., regenerator) and in the presence of about 20% water vapor and from 60 to 2000 ppm sulfuric acid (H_2SO_4).
- That the substance be stable at a temperature of 550 °C in a strongly reducing environment (i.e., reactor) and in the presence of water vapor (i.e., stripper).
- That the substance possesses a greater affinity for V than for the zeolite or the catalyst components.
- The amount of substance required for the effective protection of the catalyst must be low enough to avoid excessive dilution of the catalyst and in that way avoids loss of catalytic activity and selectivity.
- The rate of V capture must be high enough to avoid damaging the catalyst.
- The substance ought to maintain its capability to capture V while it remains within the cracking unit.
- If the substance contains metallic elements, these must not be interchanged by the zeolite cations.
- The substance must not be damaging to either the catalyst or its metallic structure.
- The substance ought to be able to be incorporated within the catalyst particle during its production (i.e., integral particle), and/or to be able to be prepared in the form of particles that are able to be fluidized having good abrasion strength, in order that they can flow together with the catalyst in the unit (i.e., dual particle).
- The substance must be cheaper than the catalyst since it is charged to the catalyst cost in order to decrease the fresh catalyst addition and in this manner to diminish the operation cost.

- It must be acceptable from the viewpoint of environmental preservation. The substance must not require particular handling conditions, it must not generate toxic materials during its preparation, nor can it be apt to be converted into a dangerous contaminant after being used.
- It must not possess dehydrogenating activity nor facilitate Ni and V dehydrogenating action.

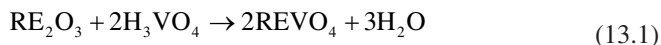
Despite a great deal of investigation, no substance has been found which meets all the requirements with respect to an ideal trap for retaining vanadium.

The use of rare earths for the preparation of V-tolerant FCC catalysts provides a way forward because of the following attributes: [24]

- They can process high metal-containing feeds.
- They can capture and immobilize V in a nondestructive form.
- They irreversibly bind V so that V cannot migrate back to the catalyst.
- They have a high capacity to remove a considerable amount of V from the catalyst.
- They show negligible interaction with other acidic species (e.g., sulfur (S) as H₂SO₄).
- Vanadium migration to the trap is significantly faster than the migration of V to the zeolite.

Metal *passivation* reduces the harmful effects of metals without substantial reduction in catalyst activity and without removing the metal from the unit. Nickel and V which constitute the most relevant poisons for catalytic cracking catalysts are usually associated metal porphyrins. Porphyrins are organometallic compounds found in the higher boiling range oil fractions, and distillation concentrates Ni and V in the fractions typically sent to the FCC unit. It is during the FCC process that the metals form a deposit on the catalyst surface, damaging the zeolite structure [19, 24]. Therefore, the use of rare earths will help reduce the deleterious effect of V and Ni.

Rare earth oxides such as La₂O₃ are basic in nature and can neutralize vanadic acid (H₃VO₄) to form rare earth vanadates [24, 55, 59, 60], thereby preventing the rapid hydrolysis of the zeolite framework. The reaction of rare earths with acidic vanadium compounds forming vanadates is represented by Reaction 13.1



where RE₂O₃ is a rare earth oxide, which leads to the formation of stable vanadium compounds [61].

Therefore, the introduction of rare earths into the zeolite helps to reduce metal poisoning and results in the retention of the aluminum framework and improved stability of the zeolite structure [10, 24, 62–72].

13.2.2 Use of Rare Earths to Improve Catalyst Stability

Most catalysts used in processes involving high severity operation, such as high temperatures and steam, face the inherent problem of hydrothermal deactivation that has to be mitigated. FCC catalysts operate between moderate to high temperatures (i.e., 500–800 °C), in the presence of steam, especially during the regeneration step. These severe conditions strongly influence the performance of the catalysts especially during catalyst regeneration which usually takes place at temperatures as high as 800 °C and in the presence of steam. With such severe conditions, zeolite dealumination becomes a real problem. For instance, USY (i.e., ultra-stable Y) zeolites used in standard FCC catalyst usually have a framework Si/Al ratio of approximately 5 before reaction and after regeneration, the equilibrium catalyst has a Si/Al ratio close to 20, showing the extent of dealumination in the FCC regenerator [20, 73]. Therefore, thermal stability and hydrothermal stability of zeolites are among the most important parameters for catalyst manufacturers.

To mitigate the problem of catalyst deactivation, rare earths can be used to improve the hydrothermal stability of FCC catalysts [5, 18, 67, 72–81]. Lanthanum and cerium (Ce) are the two main rare earths used in FCC catalysts [1, 2, 6–8, 82, 83]. These metals limit the extent to which zeolite dealumination occurs, thereby stabilizing the structure under the conditions of the FCC unit [75]. A study carried out at BASF [84] shows the differences in catalyst hydrothermal stability with and without rare earth (Fig. 13.5). Rare earth zeolite Y (REY) shows a greater thermal stability than NH_4Y (i.e., ammonium form of zeolite Y where the proton is replaced by NH_4^+ ion through ion exchange). This is because rare earths provide hydrothermal stability to the zeolite by improving retention of the catalysts' surface area, as well as inhibiting dealumination, resulting in greater preservation of the acid sites [84].

13.2.3 Effect of Rare Earths on the Activity of Catalysts

Zeolites used in cracking catalysts undergo reactions in the high-temperature steam environment of the regenerator that destroy the active sites. As catalysts age in the FCC regenerator, the unit cell size drops due to dealumination of the zeolite, through the reaction of the active sites with steam. The rare earth ions in the zeolite retard this deleterious reaction from occurring, thus preventing the collapse of the crystal structure. This active site preservation helps to maintain the activity of the catalysts. Manipulation of the active site density of the catalysts with rare earths translates into improved catalyst activity and/or selectivity profiles that are available to refiners [22].

The fact that rare earths inhibit the dealumination of a zeolite, means that a higher concentration of acid sites will be found in a rare earth ion-exchange catalyst, leading to improved activity and hydrothermal stability. On average, the acid sites

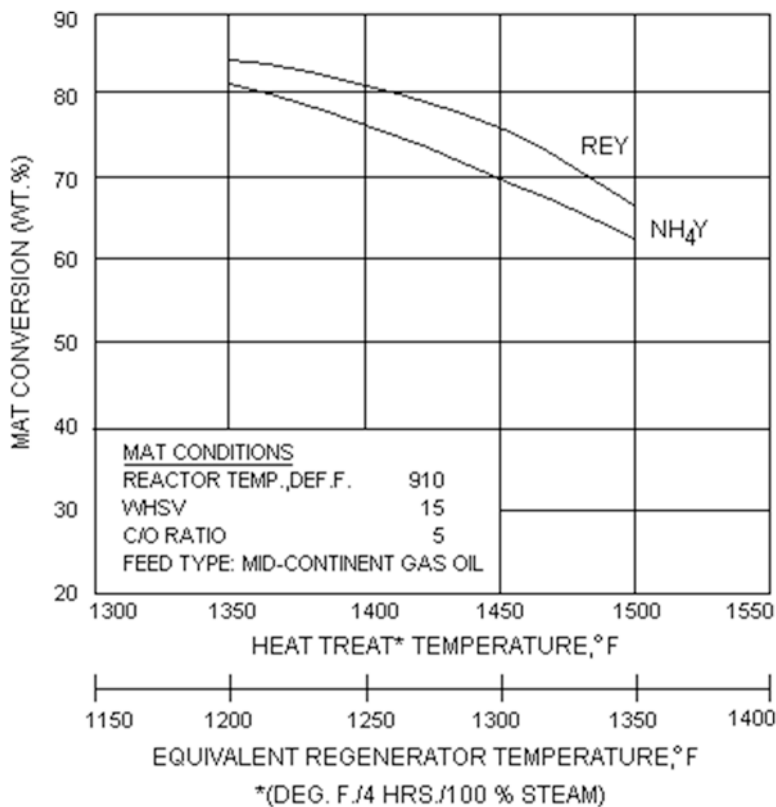


Fig. 13.5 Effect of rare earths on the hydrothermal stability of Y zeolite [84]

are weaker and in closer proximity to each other than those found in a more highly dealuminated catalyst that is characterized by lower unit cell size measurements.

As a result of the greater number of active sites, the cracking activity of the catalyst increases. Therefore, the incorporation of rare earths in catalytic cracking catalysts enhances gasoline yield. Figure 13.6 shows a plot of gasoline yield at varying conversion levels for two standard cracking catalysts with different levels of rare earths. These data suggest a strong correlation between rare earth content and gasoline yield.

Therefore, by restricting the loss of aluminum atoms from zeolite, rare earths increase the activity and gasoline yield of FCC catalysts [85].

Whether a rare earth or non-rare earth catalyst is used in the refinery operation depends on the type of feed and desired products. If a refinery is interested in processing residue feed into gasoline, a rare earth cracking catalyst will be desired.

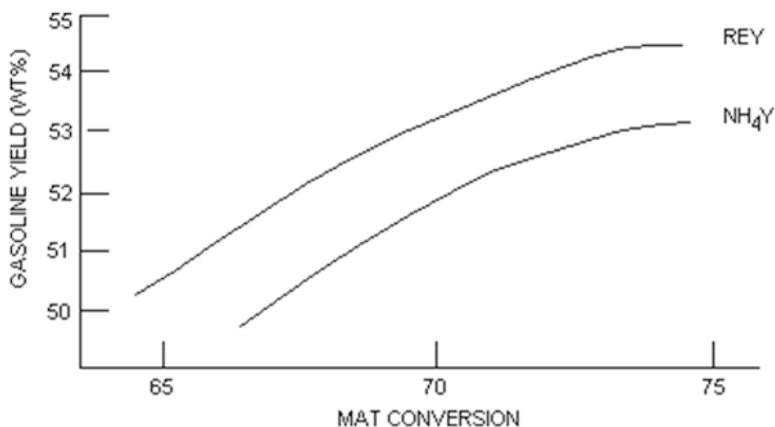


Fig. 13.6 Effect of rare earths on gasoline yield [84]

13.3 Application of Rare Earths in the Transportation Industry

From a glance, it might look as if the use of rare earths in the transportation sector is limited, but taking an in-depth look suddenly reveals the widespread use of rare earths in the automotive industry. For instance, rare earths find applications in several car parts such as windshield wipers, antilock brakes, airbags, electric windows, power steering and in the control of vehicle emissions.

13.3.1 Use of Rare Earths in Car Components

Figure 13.7 illustrates the widespread use of rare earths in the automotive industry [86], with neodymium (Nd) being the rare earth metal that is most widely used. The use of Nd was also confirmed in a study carried out by Alonso et al. [87] where approximately 0.44 kg of rare earths was estimated for use in a typical conventional sedan with approximately 80% of the rare earth content in magnets. This study also indicated that Ce, the second most widely used rare earth, was incorporated into catalytic converters.

It is expected that electrification of the automotive industry will reshape the role played by some rare earths and limit their applications as components such as catalytic converters that will no longer be required. The advent of electric vehicles (EVs) is seen as a key technology to reduce air pollution in densely populated areas. Electrification of the automotive industry will provide alternative pathways to diversification of energy, as well as contributing to reduction in greenhouse gas emissions. Coupled with the low-carbon electricity sector, electrification of the

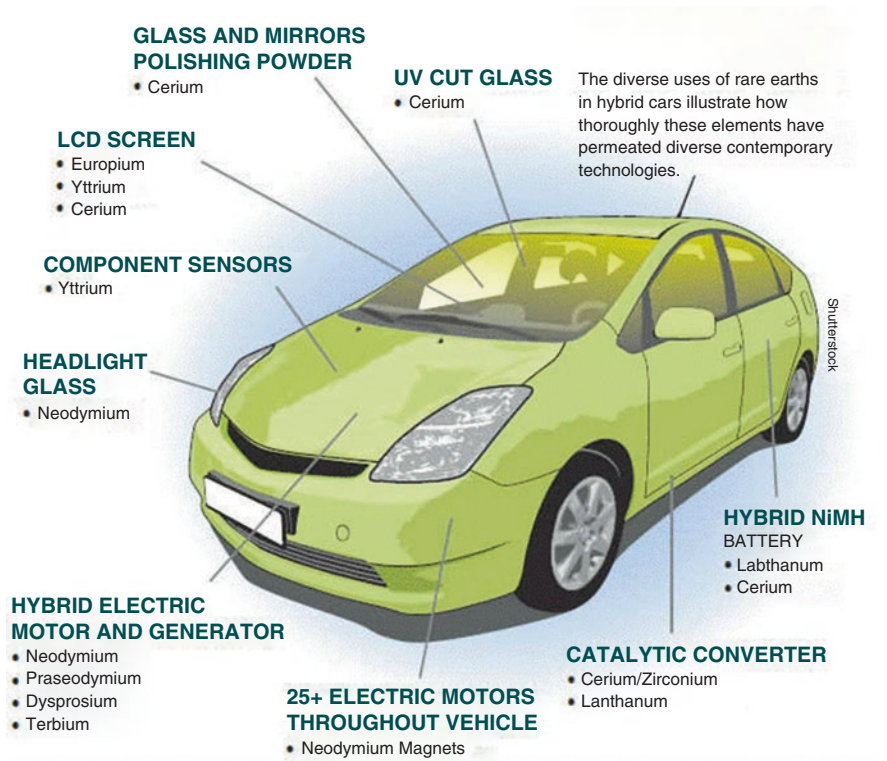


Fig. 13.7 Application of rare earths in the automotive industry [86]

automotive sector has a huge potential to reduce greenhouse gas emissions through zero tailpipe emissions and better efficiency in comparison to internal combustion engine vehicles [88].

Other rare earth applications include batteries to power the electric vehicles. These batteries will require high-efficiency magnets to convert energy to torque where the force of the spinning axle is used to power the wheels of an electric car.

The strength of a magnet is determined by its coercive force and flux density. Magnets made using rare earths such as Nd are known to have high coercivity and flux density, and it is this combination that makes them perfect for high-powered EVs. Neodymium magnets can only be used at low temperatures as they lose their magnetism at temperatures around 60–80 °C. To permit higher-temperature use, other rare earth elements such as dysprosium (Dy) and terbium (Tb) can be added, increasing operating temperatures to above 160 °C. The coercivity of the magnet can also be increased by adding Dy and praseodymium (Pr). The composition of EV magnets is approximately 24% Nd, 7.5% Dy and 6% Pr [86].

In most hybrid or EVs, around 2–5 kg of rare earth magnets are used depending on the design [87–89], primarily in the heating, ventilation and air-conditioning (HVAC) systems.

It is projected by 2030, that the growth in EVs will lead to a rise in demand for magnetic systems [88], and it is anticipated that rare earth magnets will continue to play a fundamental role in the design of the EV. Thus, the increase in demand for rare earth magnets will drive the demand for rare earths in the future automotive industry.

13.3.2 Role of Rare Earths in Catalytic Converters

A catalytic converter (Fig. 13.8) is a unit that fits into the front part of the exhaust system of a vehicle, close to the engine, to reduce the emission of gaseous pollutants, such as carbon monoxide (CO), nitrogen oxides (NO_x) and HCs. When exhaust gas from the engine enters the catalytic converter, it passes through the inner catalyst honeycomb. Here the engine exhaust gas comes into contact with catalysts that will ignite the chemical reactions needed to convert the harmful pollutants into more benign gas-phase chemical species. There are two main types of catalysts that will control these reactions: oxidation catalysts and reduction catalysts.

The catalyst formulation is comprised of three key constituents: (1) precious or noble metals (platinum (Pt), palladium (Pd) and rhodium (Rh)); (2) alumina (Al₂O₃) and (3) rare earth-based materials which enhance catalytic activity of the precious metals. Rare earths promote noble metal dispersion, increase thermal stability of the alumina support, promote the water-gas shift and the steam reforming reactions and store and release oxygen under conditions fluctuating between oxidizing and reducing. Cerium is typically used in this capacity.

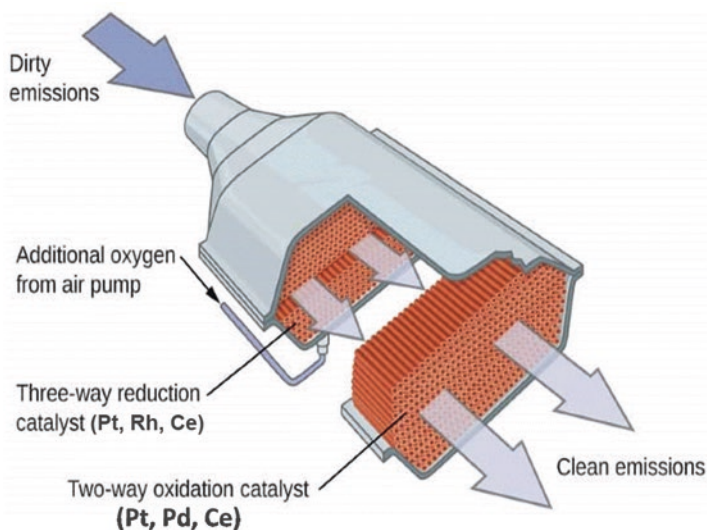


Fig. 13.8 Illustration of the catalytic converter. (Modified from Sokol [90])

Three-way reduction catalysts are designed to perform multiple oxidation and reduction reactions simultaneously, as well as convert NO_x into oxygen (O_2) and nitrogen (N_2). The two-way oxidation catalysts are designed to perform two simultaneous reactions, primarily converting CO and HCs to CO_2 and H_2O . The reason that two different types of catalysts are necessary is because CO and HCs require a lean fuel/air mixture for conversion to occur, while NO_x conversion requires a rich fuel/air mixture. Rare earths are now incorporated in catalytic converters because of the benefits that they bring.

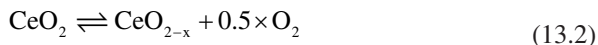
13.4 Role of Rare Earths in Environmental Protection

Rare earth such as La and Ce have been used as structural and electronic promoters in several applications in the field of environmental catalysis. For example, lanthanum oxide (La_2O_3) is used as surface area stabilizer of Al_2O_3 and zirconia (ZrO_2) support substrates [3], while cerium oxide (CeO_2) is used to increase the oxygen storage/release properties of three-way catalyst formulations. Although rare earths can be introduced into the catalyst substrate in several forms, in general, they are used in the form of oxides in catalyst formulations. Rare earths do not act alone but always in combination with other elements. Their role is, therefore, being either catalyst promoters (i.e., structural or electronic) or stabilizers to improve the activity and selectivity or increase the thermal stability of the catalyst [91]. Two application areas are combustion and air pollution control.

13.4.1 Rare Earths in Catalytic Combustion

Ceria (CeO_2) or ceria-based materials are used as a promoter due to ceria's oxygen storage capacity (OSC). Without any OSC function, the ratio of oxygen to fuel needs to be tightly controlled with a specific stoichiometric ratio to achieve the best conversion rates [92]. This is because while CO and HCs are converted to CO_2 under oxidizing conditions, the reduction of NO_x to N_2 only shows good conversion efficiency under reducing conditions. Cerium ions can easily switch between 3^+ and 4^+ oxidation states via the creation and regeneration of oxygen vacancies, which allows the ceria-containing catalyst material to store oxygen from the exhaust stream when it is in stoichiometric excess, promoting conversion of NO_x , as well as release oxygen to the exhaust stream when it is deficient, promoting conversion of CO and HCs to CO_2 . This expands the air-to-fuel ratio "window" under which acceptable catalyst performance is achieved for all three reactants. Typically, a CeO_2 - ZrO_2 blend is used to improve thermal stability. Platinum or palladium are used as the active oxidative catalyst, with Rh is included for the reduction of NO_x to N_2 [92].

The success of CeO_2 in redox and combustion catalysts is related to its ability to shift easily between a reduced and an oxidized state as a result of a change in gas-phase oxygen concentration according to the following reaction:



This allows CeO_2 to act as an oxygen buffer providing oxygen under rich conditions and removing it under lean conditions for optimal conversion in a three-way catalyst (TWC) system.

Most FCC catalysts contain zeolites or molecular sieves as active components [33]. Zeolites improve the activity and selectivity of the catalysts for the desired cracking reactions. The porous nature of the zeolites means they are susceptible to coke formation during catalysis, which leads to deactivation of catalytic activity. The catalyst will then have to be regenerated by burning off the coke. To reduce the coke content of zeolites during regeneration, the degree of coke burnoff must be increased to promote the formation of CO_2 as a combustion product, as opposed to forming CO . The formation of CO_2 rather than CO increases the amount of heat released in the regenerator and reduces the amount of pollution control treatment needed before the regenerator flue gas can be passed into the atmosphere. In addition to the degree of coke burnoff, the rate of coke burnoff in the catalyst regenerator is also important. A faster burnoff rate allows a smaller amount of catalyst to be used in the regenerator and allows the regenerator to be sized smaller than would otherwise be possible.

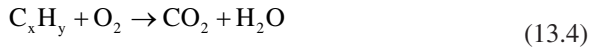
It is known that the degree of coke burnoff and the rate of coke burnoff in an FCC catalyst regenerator can be increased by adding a promoter, such as a catalytic metal, to the FCC catalyst. Rare earths have been found to be suitable promoters in FCC catalysts because they are stable and can withstand the continuous cycling between the high-temperature cracking reaction zone in the FCC system and the even higher-temperature regeneration zone [12]. In addition to their role in coke burnoff, rare earths can also help to improve product yields and reduce the amount of coke formed in the reaction zone. They are usually introduced in the FCC catalysts via ion exchange or impregnation. The amount of rare earth metals utilized is calculated on the basis of RE_2O_3 . The application alleges that catalysts promoted with the rare earth metals acquire excellent selectivity, providing a relatively high yield of gasoline and reducing coke production [23].

13.4.2 Use of Rare Earths in Air Pollution Control

Anthropogenic activities (e.g., release of greenhouse gases) have led to an increase in air pollution, leading to a major public health concern, particularly in urban areas. More stringent legislation to control and limit pollutant emissions has been proposed to combat this problem. For the automotive sector, stringent environmental legislation has led to the development of the catalytic converter technology to

control and treat these pollutants. Initially, Pt/Pd or Pt/Rh oxidation catalysts were developed to limit HC and CO emissions which were later developed into TWC systems that also converted NO_x emissions.

Although the main reactions for exhaust purification using the TWC are the oxidation of CO and HCs to CO₂ and H₂O, and the reduction of NO_x to N₂, other reactions, such as the water-gas shift reaction or reaction of pollutants with H₂O or H₂ can occur as well: [92]



Three-way catalysts consist of a monolith substrate, high surface area washcoat with oxygen storage promoter materials, the active catalyst (platinum group metals (PGMs)) and promoter materials [92, 94].

Alumina and thermally stabilized variations of Al₂O₃ are important automobile catalysts as they provide high surface area for dispersion of active PGMs as very small crystallites (e.g., initially less than 10 nm). Within a high surface area support, the PGM crystallites are dispersed which assists in mitigating their high-temperature sintering and deactivation. Alumina also absorbs poisons (e.g., S, phosphorus (P) and metals) which helps retain catalytic performance, and it also helps binding the catalyst layer to the substrate. Ceria in various forms also has several roles [92]. It has a stabilizing effect on the Al₂O₃ surface area at high temperatures, and it is also capable of stabilizing the PGM dispersion, especially Pt. In addition, CeO₂ allows for two other performance enhancing phenomena to take place: (1) oxygen storage and (2) the water-gas shift reaction (Reaction 13.6).



Ceria stores O₂ as CeO₂ (Ce(IV)) when the exhaust gas is lean (i.e., a reducing or fuel gas environment) and releases O₂ when the gas becomes rich (i.e., an oxidizing or flue gas environment), forming Ce₂O₃ (Ce(III)), and enables CO and HC adsorbed on the catalyst to be oxidized during rich excursions when there is insufficient O₂ in the gas [93]. This improves the oxidation performance of the catalyst under rich operating conditions, and leads to the production of H₂ from the water-gas shift reaction, as well as the decomposition of NO_x. Originally, CeO₂ was incorporated into the catalyst matrix. Today, various mixed ceria oxides which demonstrate enhanced stability are used. Although exact catalyst formulations are proprietary, it is clear from publications in the literature the performance of the catalyst is influenced by the forms and methods in which components are incorporated into the catalyst.

The beneficial effects of rare earth metals in exhaust catalysts have been recognized [10]. The rare earth metals promote noble precious metal dispersion, increase thermal stability of the alumina support, promote the water-gas shift and the steam reforming reactions as well as store and release O₂ under conditions fluctuating between oxidizing and reducing.

Development of TWC technology has been critical in maintaining air-quality regulations for gasoline engines via the conversion of pollutants from the internal combustion engine exhaust. The development of improved TWC formulations is an important challenge for the automotive industry. To meet increasingly stringent environmental regulations around the world, the development of more efficient catalysts will require a complete understanding of the many parameters related to TWC design.

13.5 Application of Rare Earths in the Chemical Industry

One area that is beginning to see the emergence of catalysts containing rare earths is chemical processing where the introduction of rare earths leads to increased catalyst performance.

13.5.1 Use of Rare Earths in Methanol Synthesis

Methanol (CH₃OH) is one of the most important basic industrial chemicals, with considerable potential as feed for the production of organic raw materials. Methanol derivatives end up in products such as paints, solvents, engineered wood, plastics, polyethylene terephthalate (PET) bottles, safety glass, carpets, mattress foam, fertilizer and furniture using resins. The value chain for CH₃OH is shown in Fig. 13.9.

Methanol was discovered in the seventeenth century by Robert Boyle via wood distillation [94, 95]. Boyle's process continued to be used until the beginning of the twentieth century when Sabatier introduced the first synthetic pathway for the production of methanol by reacting CO with H₂ [95]. Based on the Sabatier's synthetic process, BASF patented a syngas-based methanol production process [96], where syngas (CO, CO₂ and H₂) was supplied via coal gasification. The BASF process was carried out over a zinc oxide/chromium oxide (ZnO/Cr₂O₃) catalyst at high temperature and pressure (e.g., 300–400 °C and 25–35 MPa). As this process was highly inefficient, research efforts continued to develop and improve not only the process operating conditions, but also the catalyst and the use of cleaner produced syngas. Operating temperatures were reduced to 300 °C, and pressures to 10 MPa by Imperial Chemical Industries (ICI) in 1966 [94, 95], and then further reduced by Lurgi [94, 95] to 230–250 °C and 4–5 MPa, respectively.

Although a typical methanol synthesis catalyst mostly consists of copper (Cu), zinc (Zn) and aluminum (Al), the use of catalysts incorporating rare earth elements

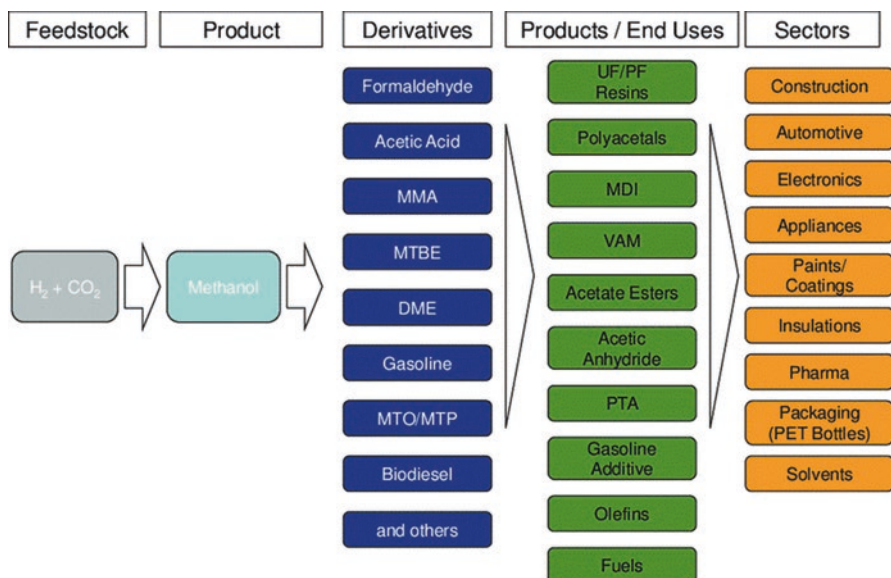


Fig. 13.9 Methanol value chain [94]

has been shown to improve the catalytic performance [94, 95]. Recent catalyst development efforts [97] show that Pd supported on La_2O_3 is an active and selective catalyst for methanol synthesis. The application of rare earths in methanol synthesis is attributed to their ability to influence the surface basicity of the catalyst. Properties such as strength of basic sites, ionic radius and electronegativity have been found to be correlated with the activity or selectivity of the catalyst. More research is needed to better understand the role of rare earths either as supports or promoters.

13.5.2 Applications of Rare Earths in Coordination Chemistry

Rare earths react with many organic molecules to form organolanthanide complexes. These complexes are increasingly being incorporated in the design and application of coordinated complexes as catalysts for polymerization and organic synthesis [98]. This has led to the development of more efficient or selective catalysts to produce high added-value stereoregular polymers or copolymers.

Rare earths are also being incorporated into metal organic frameworks (MOFs) because of their coordination chemistry [98]. Rare earth MOFs have been studied for a wide variety of potential applications, including sensing, gas adsorption, chemical separations, catalysis, drug delivery, near-infrared emission, proton conductivity, single molecule magnets and lighting applications [99].

13.6 Summary and Outlook

Rare earths are a key component of FCC catalysts, providing stability to the zeolite catalyst structure, as well as affecting the selectivity of the catalyst for specific reactions. The quantity of rare earths influences the behavior of the zeolite active component with regard to its response to the hydrothermal deactivation and contaminant metals. The presence of rare earths influences the rates of hydrogen transfer reactions, which in turn, have an impact on catalyst deactivation by coke formation.

Rare earths also find wide application in the transport industry and they are also used as catalysts for cleaner combustion and air pollution control in car exhausts.

There is also a continuous and growing interest in the application of rare earths in other fields such as methanol synthesis and coordination chemistry where the rare earths are used as supports or promoters. The challenge to fully understand the interaction mechanism between rare earths and other oxides and metals still remains. It is expected that recent developments in the field of nanotechnology, material science, analytical and characterization techniques will provide new opportunities to address this challenge and also lead to more research into new ways of designing and preparing high-performance catalysts.

The wide range of rare earth applications will subsequently lead to an increase in their demand. As the demand for rare earth catalysts continues to grow, the tendency to generate more spent catalysts also increases. The current practice is to send spent catalysts to landfills, which is not sustainable. Therefore, it is important to develop a recycling strategy for spent catalysts as well as recovery techniques for rare earths.

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