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Application of rare earths in fluid catalytic cracking: A review

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Abstract: The need for more active and hydrothermally stable fluid catalytic cracking (FCC) catalysts to combat the effect of metal contaminants has led to an increase in demand for rare earth oxides. Rare earth oxides enhance catalyst activity and prevent the loss of acid sites during the FCC unit operation, especially when heavy residue with high metal content is used as feed. In this paper, a review was carried out to show the effects of rare earth elements on the structure, activity, and stability of FCC catalysts. Also, the use of rare earth elements as vanadium traps was analyzed in conjunction with the mechanism of catalyst deactivation by vanadium. The objective was to elucidate the interaction of vanadium species with the zeolite component of the FCC catalysts and the role of rare earth elements in countering the deleterious effects of vanadium on the FCC catalysts.

Keywords: FCC catalyst; rare earth; vanadium trap; zeolites

1 Introduction

1.1 Applications of rare earth elements

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, lanthanum, and yttrium 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 100000 t annually as shown in Table 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, among a myriad of applications[1,2,6–8]. Their numerous applications have led to an increase in demand for rare earths.

1.2 Rare earth market

The major end uses of rare earth oxides and catalysts are shown in Tables 1 and 2. Based on the work carried out by Goonan[2], and summarized in Table 1, 27380 t of rare earth oxides were used as catalysts for fluid cracking (72%) and automobile catalytic converters (28%). For rare earth application in catalyst, La_2O_3 contributed 66%; CeO_2, 32%; Nd_2O_3, 0.8%; and Pr_6O_7, 0.6%. Other catalyst uses include those for air pollution control and chemical production.

From Table 1 it can be seen that the market share for catalysts was 21% in 2008[2]. Also, the catalyst market accounted for 47% of the consumption of La_2O_3 (of which 98% went to fluid cracking and 2% went to automobile catalysts), 21% of the consumption of CeO_2 (of which 78% went to automobile catalysts and 22% went to fluid cracking), 1.7% of the consumption of Pr_6O_7 (100% of which went to automobile catalysts), and 1% of the consumption of Nd_2O_3 (100% of which went to automobile catalysts)[2].

The projected demand for rare earths in 2016 is summarized in Table 2[9]. From Table 2 it can be seen that the major destination for rare earths is China, which accounts for a whopping 65% of the rare earths demand. There is also a drop in the market share of the catalyst industry to 16% compared to 21% in 2008.

The demand for rare earth elements is a direct result of their applications in the end-use products, such as flat panel displays, automobiles and FCC[7]. This means the strength of the demand of the final products for which they are inputs, influences the demand for rare earths.

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Table 1 Global rare earth consumption by market sector for 2008

Rare earth oxide	Amount by Market Sector/t									
	FCC catalyst	Automobile catalytic converters	Ceramics	Glass	Metallurgy	Magnets	Battery alloys	Phosphors	Other	Total
CeO_2	1980	6840	840	18620	5980		4040	990	2930	42220
Dy_2O_3	–		–	–	–	1310	–	–	–	1310
Eu_2O_3	–		–	–	–	–	–	441	–	441
Gd_2O_3	–		–	–	–	525	–	162	75	762
La_2O_3	17800	380	1190	8050	2990		6050	765	1430	38655
Nd_2O_3	–	228	840	360	1900	18200	1210	–	1130	23868
Pr_6O_7	–	152	420	694	633	6140	399	–	300	8738
SmO	–		–	–	–	–	399	–	150	549
Tb_6O_7	–		–	–	–	53	–	414	–	467
Y_2O_3	–		3710	240	–	–	–	6230	1430	11610
Others				480						480
Total	19780	7600	7000	28444	11503	26228	12098	9002	7445	129100

Table 2 Forecast global rare earths demand for 2016 (t)

Application	China	Japan & SE Asia	USA	Others	Total	Market share/%
Catalyst	15500	2500	5500	1500	25000	16
Ceramics	4000	2500	2250	1250	10000	6
Glass	7000	1000	1000	1000	10000	6
Metallurgy	23000	3000	2000	2000	30000	19
Magnets	28000	4500	2000	1500	36000	22.5
Phosphors	8500	2000	750	750	12000	7.5
Polishing	13000	13000	2000	2000	18000	11
Other	5000	4000	8000	2000	19000	12
Total	104000	21500	23500	11000	160000	100
Market share/%	65	13	15	7	100	

Catalysts represent a large market for rare earths where they provide properties desired for effective catalysis such as in FCC and in automotive catalysts[1].

2 Rare earths in FCC catalysts

Rare earth oxides have been widely investigated in catalysis as structural and electronic promoters to improve the activity, selectivity and thermal stability of catalysts[1,2,10–29]. As can be seen from Table 2 catalysis plays a major role in the consumption of rare earths with the FCC playing a major role in the catalytic application of rare earths. Rare earth application in FCC emerged in the early 1960s when zeolites were introduced as cracking catalysts for oil refining. 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, are used in cracking catalysts to refine crude oil into gasoline, distillates, lighter oil products and other fuels. They are also responsible for eliminating leaded gasoline. The use of these lanthanide fluidized cracking catalysts also promotes very energy efficient petroleum cracking.

In this article, the role of rare earths in FCC catalyst was reviewed with the goal of highlighting how the presence of rare earths helps in maintaining catalyst effectiveness vis-à-vis the hydrothermal stability and the product distribution. The mechanism of catalyst deactivation by vanadium was also presented to better understand the interaction of vanadium with rare earths under FCC operating conditions.

2.1 FCC catalyst composition

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 (zeolite), a matrix such as amorphous silica-alumina (which also provides catalytic sites and larger pores), a binder (such as be tonite clay) and filler as illustrated in Fig. 1[30]. It is composed of spherical particles, suitable for application in a fluidized circulating reactor, in which the zeolite crystals are dispersed in an active matrix of alumina or silica-alumina together with clay particles. The spherical particles contain large voids and pores necessary for allowing the mass transport of the heavy feedstock.

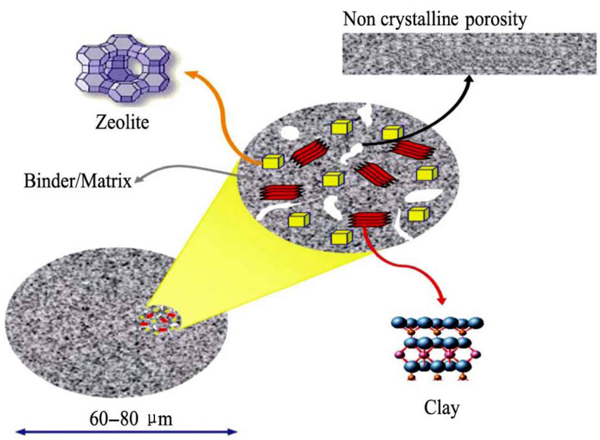

Fig. 1 Schematic representation of FCC catalyst