ZEOLITE CRACKING CATALYST

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ABSTRAC

Nowadays, refiners are facing a continuing need to add bottom processing by catalytic process (catalytic cracking and hydro cracking processes) capacity a result of gradually deteriorating crude oil quality and flat-to-declining for residual fuel oil.

Catalytic cracking process of heavy feedstock converts it into light products (gasoline, kerosene and diesel oil) using an acid cracking catalyst (silica alumina amorph and zeolite). Improvemements in cracking catalyst have concentrated on zeolite improvement by catalyst matrix technology.

Advantages of cracking catasyst matrix technology, and catalyst deactivation are described briefly.

I. INTRODUCTION

Nowadays, refiners are facing a continuing need to add bottom processing by catalytic process (catalytic cracking and hydro cracking processes) capacity as a result of gradually deteriorating crude oil quality and flat-to-declining demand for residual fuel oil.

Catalytic cracking is the most important and widely used refining for converting feedstock from heavy distillate to residue into valuable gasoline and lighter products such as propylene, butylenes, amylene and isobutene used as feedstock of alkylation and polymerization processing and oxygenate octane booster production using acid silica-alumina amorph and zeolite catalyst.

Production of the high yield and octane number of this cat. cracked gasoline from the low quality feedstock (such as residue with high boiling range, high aromatic content and high impurity) needs a high operating condition (i.e. high feedstock conversion, high operating temperature and high oil recycle ratio) and uses a high catalyst performance.

There are two units of catalytic cracking process (fluid cracking, riser cracking) with over 103,5 MBPSD total capacity in Indonesia (ASEAN 280.0 MBPSD) processing vacuum distillate (15.8 vol.%) and atmospheric residue (84.2 vol.%) using zeolite catalyst. Make up catalyst is about 20.0 tons per day of fresh catalyst[1].

Catalyst type, feedstock, and reactor temperature influence a gasoline molecular type and octane number. Optimum selection of these variables can result in octane barrel of gasoline. Zeolite unit cell size is the key catalyst parameter controlling the octane number of gasoline. Low K-factor (high aromatic) feed produce gasolines of higher octane numbers as compared to high K-factor (paraffinic) feedstock.

Operation in overcracking regime results in significant increase in octane number due to cyclization reaction and H-trasfer of cycles in the C_8-C_{10} range aromatics. This will also increase the production of high value C_3 and C_4 olefins which are also useful for producing alkylates and oligomers[2].

Zeolites are microporous materials used largely in cracking catalyst because of their higher surface area, adsorption, confinement, and molecular new properties. Improvements in FCC catalyst have concentrated on zeolite improvement by catalyst matrix technology. Advantages of FCC matrix technology and catalyst deactivated are described briefly.

II. ZEOLITE AS CRACKING CATALYST

Many variation in composition of silica-alumina cracking catalysts have been used but the standards catalyst for a long period contained 13 wt.% alumina and 87 wt.% silica. Increasing the alumina content to 27 wt.% gives a more active and also more expensive catalyst. The high activity of zeolite cracking catalyst permits short residence time cracking. Activity of natural zeolite can be increased by chemical reatment (Table 1)[3]. Catalyst type can effect gasoline composition to a marked degree.

Table 1
Performance of treated natural mordernite

Chemical		Surface Area, m^2/g	Acidity, mmol NH_3/g
N_2OH	Non-treated	35.02	4.231
	Treated	98.2	6.642
HCl	Non-treated	180.01	2.6588
	Treated	251.7	4.4062
NH_4NO_3	Non-treated	180.01	2.6588
	Treated	220.3	4.4518

Table 2
Activity of steam deactivated cracking catalyst

Feedstock Conversions, wt.%	Gasoline Product Yield, wt.%
$45.0^{(x)}$	20.6
42.7	20.6
41.9	28.0
40.0	28.3
36.5	32.3
34.0	29.3
31.9	27.0
30.6	25.0

Note: $^{(x)}$ = Fresh catalyst

Improvement in FCC catalyst have concentrated on zeolite improvement. Many advantages seen with modern FCC catalyst resulted from improved catalyst matrix technology.

The term *matrix* refers to the non-zeolite component of the catalyst. Although zeolite provides most of the cracking activity, matrix fulfills both physical and catalytic functions that contribute to catalyst performance. A major function of the matrix is to bind the zeolite crystallites together in a microspherical catalyst particle hard enough to survive interparticle and reactor wall collisions in a commercial FCC units. The presence of large (>20 A^0) pores in the matrix allows it to serve as a diffusion medium for feedstock molecules and cracked products. It facilitates heat transfer during cracking and regeneration, thus protecting the zeolite from structural damage[4]. Steaming of non-matrix cracking catalyst can reduce the catalyst activity (Tabel 2)[5].

In fact, several FCC matrix technology inovations over the last 29 years have led to improved gasoline yields, improved zeolite stability, enhanced bottoms cracking, and improved metals tolerance properties of the FCC catalyst.

Improvements in catalyst attrition resistance have enable a FCC units to operate with reduced catalyst addition to maintain activity and lowered particulate emissions from cat. crackers. Up to 30% reduction in catalyst addition rates in commercial units has been reported

Table 3
Effect of zeolite content on attrition resistance

Relative Zeolite Content	Attrition, Devision Index (D1)		
	Silica Alumina Gel	Silica Hydrosol Process	Silica Hydrosol New Process
0.12	19	8	-
0.22	30	8.2	-
0.28	32	8.5	-
0.38	34	8.8	5.2
0.50	-	9.0	5.2
0.75	-	11.2	5.2
1.00	-	16.0	5.4

Table 4
Advantages of low and high activity matrix

Low Activity Matrix	High Activity Matrix
▪ High gasoline selectivity	▪ Better bottom cracking
▪ Low coke and dry gas yields at constant conversions	▪ Improved activity in the presence of V
▪ Low coke and H_2 yield in the presence of Ni	▪ Synergistic interaction with zeolite resulting in improved stability and activity ▪ Improved LCO quality ▪ Improved MAT activity with high N_2 feeds

due to the use of attrition-resistance alumina-sol/ clay matrix technology. Effect of zeolite content on attrition resistance is shown in Table 3[4].

Increased retention of active fresh catalyst enables maintenance of unit activity with reduced additions. Pilot plants results have demonstrated a five-fold increase in zeolite activity to produce high octane gasoline and increase alkylate due to the use of improved matrix technology. This was attributed to the matrix role in retarding zeolite dealumination during steaming.

A matrix with high specific activity (activity per unit survace area) has been developed for selective bottom cracking. Pilot plant results in the presence of 5, 000 ppm contaminant metals have shown 15% to 20% reduction in coke and dry gas yields and about 5 vol.% higher gasoline plus distillate due to use of a matrix that interacts strongly with contaminants metals and passivates them. Advantages of low and high sensitivity matrix is shown in Table 4[5].

Migrations of sodium ions from zeolite into the matrix at high temperatures have been suggested as the cause of improved stability. Modern FCC contains Y-faujastie zeolite embedded in an inorganic oxide matrix. Matrix can also increase thermal and hydrothermal zeolite stability. For example, a silica alumina gel matrix dramatically improved the stability of REHY zeolite to hydrothermal deactivation. The Y and ZSM-5 zeolites are used together as catalyst in FCC units to achieve high bottom conversions with high yields on gasoline, propylene, and butene[6].

A clay-based matrix technology exhibiting higher cracking activity per unit surface area than conventional silica alumina matrixes has been described. Modal pore diameter of conventional silica alumina matrix increases with steam deactivation. However, modal pore diameter of the clay-based matrix does not change with steaming. These catalysts are also reported to maintain a near constant ratio of zeolite to matrix survace area during dectivation. As a result they are described as providing selective bottoms cracking. Commercial zeolite cracking catalysts are given in Table 5[7].

III. DEACTIVATION OF CRACKING CATALYST

Sulfur, basic nitrogen comounds, sodium, vanadium,

Table 5
Commercial zeolite cracking catalyst

Catalyst Supplier	Bulk Density Compacted, g/cc	Carrier Support	Active Agents
AK ZO Nobel	0.70 0.65-0.80 -	Active matrix Silica/alumina SiO_2/Al_2O_3	Zeolite Al, Si Zeolite, activated matrix ZSM-5
Catalyst & Chemical Industries Co, Ltd	0.72 0.70	Silica/ alumina Silica/ alumina	Ultra stable zeolite Dealuminated ultrastable Zeolite low alumina matrix
Engelhard Corp.	0.90	SiO_2/Al_2O_3	ZSM-5 In Situ USY
Grace Davision	0.75	SiO_2/Al_2O_3	Z-14 US Modivied Z-14 US
Interlat Inc.	0.50	Patent	ESM-5 Modivied ZSM-5
Instituto Mexicano Del petroleo	0.90	Amorphous alumina Silica	Zeolite rey
Mobil Chemical International Ltd.	-	Patent	ZSM-5

iron and copper in the heavy feeds of cracking process act as poisins to cracking catalyst[8].

Sulfur, for instance, has little effect on the present alumina silicate catalysts, although it may effect the older natural clay catalysts, prresumbly from formation of iron in the structure.

The acid function of cracking catalyst is sensitive to poisoning by nitrogen bases in the feedstock. Cracking activity of this catalyst can stand some nitrogen and one may actually prepare a certain nitrogen content concentration for stable operation. The effect of nitrogen content of feedstock on the reaction temperature required to maintain a constant cracking activity is higher for amorph type than that for zeolite type.

Sodium deposition of the order of 1 wt.% on catalyst gives no appreciable effects. Sodium on the cracking catalyst is known to decrease the stability of the catalyst texture in thermal of hydrothermal treatments.

Vanadium deactivates cracking catalyst by destroying the catalyst zeolite component. Zeolite destruction begins in the regenerator, where the combination of an oxidizing environment, high temperature and steam can form vanadic acid. The acidic attachment causes zeolite pores to collapse with loss of surface area and acidity. Since vanadium deactivation is essentially an attachment on the zeolite, a typical approach to improve vanadium tolerance has been addition of basic materials included alkali earth metals (Mg, Ca, Sr, Ba), alumina, phosphour, and barium titanate.

A permanent deactivation of cracking performance occurs when metals (nickel, vanadium, iron, and copper) are deposited on the catalyst. The vanadium is deposited in the form of a film on the outside of the grain (pore mouth poisoning or heterogenous pore poisoning) while nickel penetrates more deeply to inside of grain (uniform poisoning or homogenous pore poisoning). Heterogenous pore poisoning gives lower pore effectiveness than does the homogenous pore poisoning.

Accunmulation of these metals on the catalyst gives rise to the development of dehidrogenation activity of catalytic cracking catalytic leading to increased formation of gases and coke at the expense of gasoline yield. It can be inferred that nickel is about four times as harmful as vanadium. If the metallic concentrations the cracking catalyst are expressed in ppm then the effect is a function of: Cu + Fe + 4V + 14Ni. If the sum is greater than 1,000 ppm the cracking catalyst is badly contaminated. The catalyst replacement rate using resid feeds responsible for desreaced liquid yields and increased hydrogen and coke yields. The treating agent which is an oil soluble compound containing antimony, deposits contaminant metals on the catalyst and deactevates them into poorer dispersion without deactivating the catalyst. The most important metals that have effect on the formation of catalyst coke and hydrogen are nickel, vanadium and iron. It appears that the presence of antimony is important. For example, when 0,5 wt.% antimony was deposited, gasoline yield increased by 22%, and hydrogen yield decreased by 57%. For this reason, catalysts with large pores, low surface area matrices would be better for nickel tolerance. However, these catalysts have less than the optimum matrix activity for cracking and are only appropriate when nickel tolerance is the sole objective.

A recent trend in catalytic cracking is to incorporate also other catalytic functions in the catalyst, in particular to promote the burning of CO to CO2 during regeneration. These CO burning promotors, which consist, for instant of minute quantities of platinum group metals, may be incorporated in the manufactured catalyst, or the may be added as a solid or liquid additive during operation.

IV. CONCLUSIONS

Catalytic cracking processes of heavy feedstock (heavy distillate, residue) using an acid cracking catalyst (silica-alumina amorph and zeolite) is extremely efficient in producing high octane gasoline and middle distillate with significant high olefin yield for motor fuel alkylation or oxygenates productions.

Inovations and developments in matrix technology have led to improved gasoline yields, reduced catalyst usage, increased zeolite activity, and enhanced bottoms cracking and metals tolerance properties.

One of the reasons for wide acceptance of this matrix technology was the superior yields and selectivity obtained commercially with the catalysts.

REFERENCES

1. Nasution A.S., Jasjfi E., *Survey on Gasoline Production and Impact of More Stringent Specification on Catalyst Performance in ASEAN Refineries,* Paper presented in ascope Refining Workshop, Bangkok, Thailand, Noveber 10-11, 1995.
2. Badoni R.P., Umar Shanker and Kumar Y., *FCC as Mother Unit for Octane Enhancers and Petrochemicals,* Proceeding, ASCOPE'97 Conference, Jakarta, November 24-27, 1997.
3. Nasution A.S., Chairil A., and Jasjfi E., *Current Uses and Future Challenges for Zeolite in the*

Indonesian Oil and Gas Processing Industry, Paper Presented in the Joint Murdoch University-Gadjah Mada University Seminar, Perth, Australia, May 4-5, 1998.

4. Rajagopalan K., and Habib E.T. Jc., *Select Catalyst Support Properties Needed for Gas Oil or Resid Cracking,* Hydrocarbon Processing, September 1992, pp. 43-46.
5. Nasution A.S., Jasjfi E., Evita H. Legowo and Hono Witono, Pengoptimalan Aktivitas Katalis Perengkah dengan Deaktivasi Uap, Disajikan pada Seminar Nasional Teknologi Proses Kimia 2000, TGP-FT-University of Indonesia, Depok, 21 March 2000.
6. Corbert, R.A. *Restructuring Advanced Technology Mark Catalyst Activities,* Oil and Gas Journal, November 14, 1998,pp. 83-91.
7. Rhodes, A.K. *Worldwide Catalyst Report, Catalyst Suppliers Consolidate Further,Offer More Catalyst,* Oil and Gas Journal Special, October 2, 1995, pp. 35-79.
8. Harris J.R., *Use Desalting for FCC Feedstocks,* Hydrocarbon Processing, August 1998, pp. 63-68. •