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Catalysis Today 73 (2002) 49–55

CATALYSIS TODAY

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The development of catalytic cracking catalysts: acidic property related catalytic performance

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Received 9 May 2001; accepted 28 September 2001

Abstract

To meet the requirements for improving fluid catalytic cracking (FCC) yield structure and gasoline quality, a variety of novel FCC catalysts have been developed. The development is closely related to the different approaches to the modification and fine-tuning of the catalyst acidic properties. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic cracking; FCC; Cracking catalyst; Acidic property

1. Introduction

The fluid catalytic cracking (FCC) process is one of the major workhorses in refineries for the production of motor fuels. The main challenges facing FCC technologies in recent years are: processing heavier feed stocks, changing yield structures from maximized production of gasoline to LCO or LPG, and, more recently, improving product quality, especially gasoline quality. The hydrocarbon cracking is an acid-catalyzed reaction and the catalysts used for FCC process are basically acidic catalysts. Since the Y zeolite based catalysts adopted by the refiners for their FCC units in early 1970s, the major change in the acidic property of the catalysts has been the decrease of the acid site density through reducing the unit cell size of Y zeolite, to meet the requirement for cracking resid blended feedstock. For meeting the requirement of environmental issues and the changing demand of the market, refiners need different novel catalysts with improved performances such as enhancing resid cracking ability, increasing LCO yield, reducing gasoline olefinicity, decreasing gasoline sulfur content, etc. One of the approaches in Research Institute of Petroleum Processing (RIPP), to the R&D of new FCC catalysts is the modification of its acidic properties including acid site density, acid site distribution, acid strength, and acid type.

2. Resid cracking

The resource of the crude oil and the refinery profit forces the refiners to process more and more vacuum resid (VR) in their FCC units. The resid blending percentage for the world is around 25% in average, whereas in China it attains a level as high as 35% in average. The percentage will be further increased continuously both in China and in the world. Daqing oil field produces about 35% of the total crude oil output in China. The crude is paraffinic, relatively heavy, and consists of about 70% atmospheric residue (AR). Since 1980s, many refineries in China have been processing 100% Daqing AR without any pretreatment.

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PII: S0920-5861(01)00517-X

Table 1
The main properties of Daqing VR

Carbon residue (wt.%)	8.2
Ni + V (ppm)	7.67
H/C (w/w)	1.79
Aromatics + resin	58.1

Table 2
The pilot test results of DVR-1 catalyst using Daqing VR as feedstock

	Feed			
	100% VR		75% VR	
Reaction pressure (MPa)	0.15		0.15	
Reaction temperature (°C)	510		510	
Residence time (s)	1.9		1.9	
C/O	6		6	
Recycle ratio	0	0.11	0	0.09
Yields (wt.%)				
Dry gas	3.67	3.82	3.19	3.32
LPG	14.28	16.51	15.56	17.40
Gasoline	42.59	44.19	46.98	49.72
LCO	17.49	23.50	16.74	20.06
Slurry	11.31	0	8.78	0
Coke	10.12	11.48	8.05	9.01
Loss	0.54	0.50	0.70	0.49
Conversion (wt.%)	71.20	76.50	74.48	79.94
LPG + gasoline + LCO (wt.%)	74.36	84.20	79.28	87.18

The new challenge for those refiners is whether it is possible and economically effective to process 100% Daqing VR [1]. Table 1 shows the main properties of Daqing VR [2]. Obviously, the process technology and equipments are extremely important for processing such a feedstock with high carbon residue and high viscosity.

The catalyst used for resid cracking should possess bottoms cracking ability, metal tolerance, coke and dry gas selectivity, etc. In short, it should have high performance in good yield of valuable products at reasonable catalyst consumption. For resid cracking, both thermal and catalytic functions are important for the conversion of the precursors of Conradson carbon, such as asphaltenes, resins, polynuclear aromatics, etc. The distribution of the acid sites with different acid strength is a key point for achieving high resid conversion and good product yield. The total acid sites on the surface of the catalysts can be divided into two types according to the ranges of their acid strength: strong acid sites and weak acid sites. The definitions for “strong” and “weak” acid sites are based on an ammonia adsorption–desorption method used in our laboratory, in which the temperature for both adsorption and desorption is 448 K. The amount of ammonia desorbed at the temperature is taken as the measure of the amount of weak acid sites and the remaining amount of adsorbed ammonia is taken as the amount of strong acid sites. This simple method is quite effective and useful for the characterization of acidic properties of practical FCC catalysts. The catalyst design is based on, besides the pore architecture, the distribution of two different acid sites on the surface of zeolite and matrix. A new resid catalyst has been developed for 100% VR conversion with a commercial name DVR-1 [1]. The catalyst possesses abundant pores in the range of diameter 8–12 nm in its matrix and also meso-pores in its USY zeolite component. The catalyst DVR has higher amount of weak acid sites and lower amount

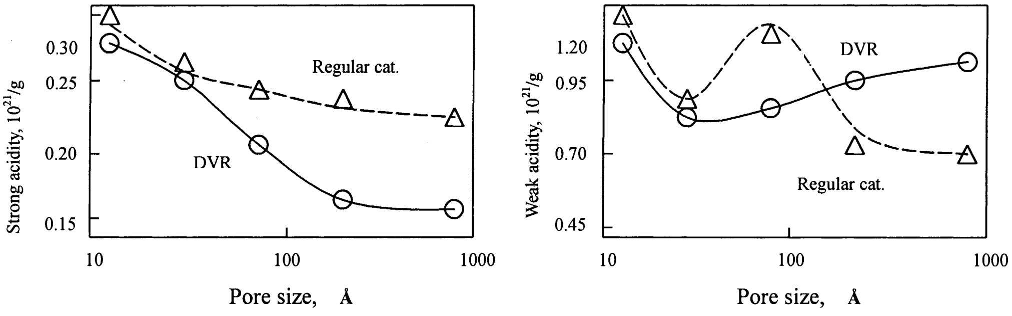

Fig. 1. The comparison of different acid site distributions for DVR and a regular catalyst.

of strong acid sites for its large pores by formulating the matrix by specially pretreated components. Fig. 1 shows the comparison of the different acid site distributions for DVR catalyst and a regular resid cracking catalyst. Hence, it exhibits good coke selectivity and resid cracking ability. The test results in a pilot plant are listed in Table 2. The catalyst has been commercially applied in a 800 kt per year VRFCC unit of Yanshan Petrochemical Corporation in Beijing. The unit was started in 1999 and displayed excellent performance in resid conversion and product yield [1,2]. The total yield of LPG, gasoline, and LCO achieves a level higher than 80 wt.%.

3. LCO yield enhancement

The increasing market demand of diesel fuel forces refiners to find ways for enhancing the LCO yield of their FCCUs. The catalyst design related to this application is focused on the adjustment of acidic properties of the zeolite component and matrix. For achieving higher LCO yield, it is proved in RIPP’s laboratory that the strong acid sites must be greatly diminished and the weak acid sites should be remained. A number of the methods can be used for the required acidity modification including the incorporation of alkaline earth metal oxides into the zeolite component [3]. One of the effective ways in acidity modification is the incorporation of alkaline earth metals or their compounds into zeolite components rather than into matrix (Table 3). For catalyst design, it is preferable that more than 40% of the strong acid amount of the zeolite should be diminished and more than 90% of the weak acid amount of the zeolite should be reserved. A specially formulated catalyst, MLC-500, has been developed and commercially used for a maximized distillate production process. The process technology is characterized in split injection points along the riser for: an untreated AR as feed, cycle oil, and a quenching media, respectively. The catalyst and the process was commercially applied in a 500 kt per year unit in Changzhou Refinery located in Hebei Province. The results listed in Table 4 show that the LCO yield has been increased by 8.6 wt.% at the expense of gasoline and slurry [1,4].

Table 4
Commercial results of MLC-500 catalyst used for maximized distillate production

	Reference catalyst	MLC-500
Feed density (g/ml)	0.8994	0.9005
CCR (wt.%)	6.3	6.9
Basic N (ppm)	1518	1700
Product yield (wt.%)		
Dry gas	6.02	5.01
LPG	10.30	11.69
Gasoline	35.15	29.78
LCO	29.09	37.71
Slurry	6.90	3.07
Coke	11.63	11.87
LCO/gasoline	0.83	1.27

4. Gasoline olefin reduction

A fairly large part of the gasoline pool for supplying the vehicle fuel market directly originates from FCC processes. FCC gasoline quality is critical for

Table 3
The distribution of acid strength modified by incorporating alkaline earth metals

	Acid amount (mmol/g)		Change of acid amount (%)	
	Strong acid	Weak acid	Strong acid	Weak acid
USY	0.74	2.60	Base	Base
6.1 wt.% MgO incorporated from $MgCl_2$ solution	0.40	2.41	−45.9	−7.3
24.8 wt.% MgO incorporated from MgO slurry	0.23	2.01	−68.9	−22.7
0.5 wt.% MgO incorporated from $MgCl_2$ solution	0.60	2.56	−18.9	−1.54
6.7 wt.% CaO incorporated from $Ca(NO_3)_2$ solution	0.32	2.31	−56.8	−11.2
REHY	1.10	3.10	Base	Base
7.9 wt.% MgO incorporated from $MgSO_4$ solution	0.40	2.53	−63.6	−18.4

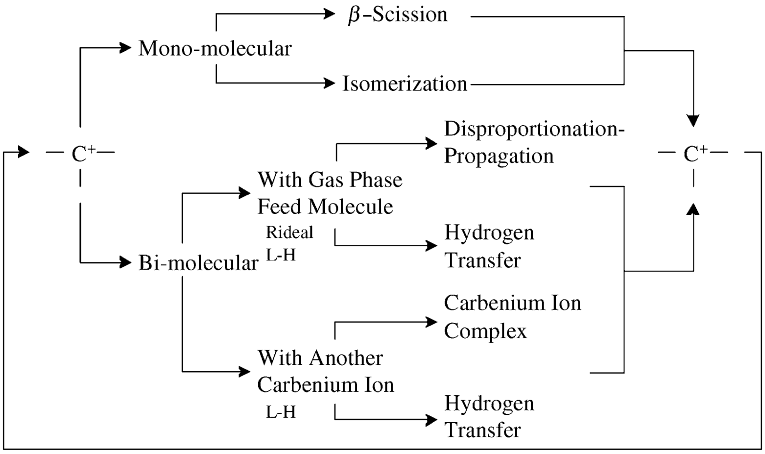

Fig. 2. Carbenium ion based mono-molecular and bi-molecular reaction pathways.

many refiners to meet the more and more stringent gasoline specifications. FCC units are expected to produce gasoline with reduced contents of olefins, aromatics, benzene, sulfur, etc., and meanwhile, still with high octane number. The concept of RIPP's research project is based on a proposed reaction scheme which separates the reaction pathways starting from carbenium ions into two main parts: mono-molecular pathways and bi-molecular pathways [5,6], as shown in Fig. 2.

The bi-molecular hydrogen transfer reactions are important for the reduction of olefin content and obviously related to the acid site density. The cracking of *n*-hexane has been studied over different zeolites in our laboratory to correlate zeolite acidic property with the selectivity of bi-molecular reaction pathways. Based on the chain mechanism, the initiation steps and termination steps of the chain reactions are both mono-molecular reactions, whereas the chain propagation steps are bi-molecular reactions. In *n*-hexane

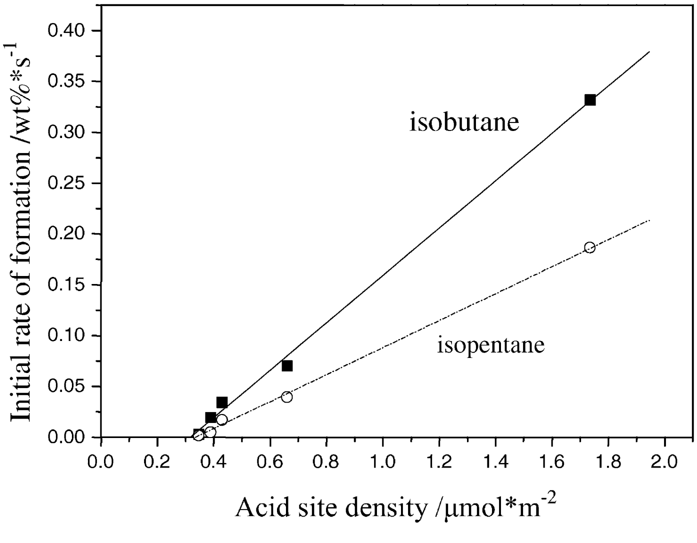

Fig. 3. Initial rate of *iso*-butane and *iso*-pentane formation and acid site density.

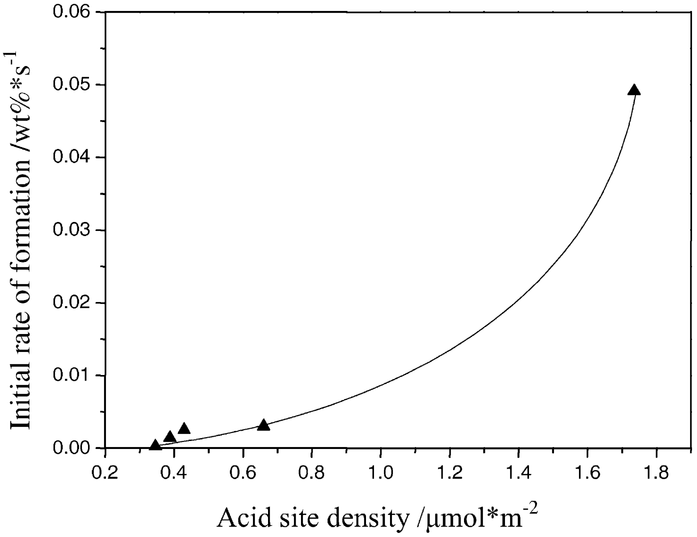

Fig. 4. Initial rate of coke formation and acid site density.

cracking, the products *iso*-butane and *iso*-pentane are both typically from bi-molecular reactions [5,6]. A well-correlated linear relationship exists between acid site density and the initial formation rates of products of hydrogen transfer reactions (Fig. 3). However, the rate of coke formation seems to be related in second order to the acid site density (Fig. 4). The reaction between adjacent carbenium ions and its role in coke formation has already been evidenced [7]. For reducing the gasoline olefinicity meanwhile maintaining coke selectivity, a new series of catalysts, GOR, has been carefully designed based on a concept of "selective hydrogen transfer", by adjusting the acid site density and modifying acid strength. By a special method for incorporating rare earth and combined chemical modification, the Y zeolite used for GOR series catalyst possesses stable unit cell size and high performance in coke selectivity. The catalysts have been commercially applied in a 1400 kt per year unit (S3) in Shanghai Refinery in 1999 and a 1400 kt per year unit (Y3) in Yanshan Refinery, Beijing in 2000. The commercial results in Tables 5 and 6 show that, for a unit with a feedstock blended with up to 60% vacuum residue, the quality of FCC gasoline has been significantly improved in the increase of *iso*-alkane content and the decrease of olefin content, meanwhile the LPG plus liquid yield and gasoline octane remain the same. The gasoline olefin contents can be reduced by 10–12 wt.% with a slightly higher coke yields.

Table 5
Product distribution (wt.%) of Y3 FCCU and S3 FCCU

	Y3 FCCU		S3 FCCU	
	Base	GOR-DQ	Base	GOR-Q
Dry gas	3.37	3.16	3.79	4.30
LPG	16.15	21.37	15.44	18.63
Gasoline	41.40	38.70	44.14	44.69
LCO	27.17	24.26	22.57	21.15
Slurry	3.67	3.54	4.64	1.73
Coke	8.24	8.97	8.92	9.00
Conversion	69.16	72.20	72.79	77.12
LPG + GSL + LCO	84.72	84.33	82.15	84.47

Table 6
Gasoline properties of Y3 and S3 FCCU

	Y3 FCCU		S3 FCCU	
	Base	GOR-DQ	Base	GOR-Q
FIA olefins (vol.%)	54.30	42.43	43.8	34.4
iso-Alkanes (wt.%)	27.06	32.89	32.71	35.80
RON	90.2	90.5	90.4	89.8
MON	79.4	79.8	79.6	80.4
Ind. period (min)	362	635	639	1005

5. Gasoline sulfur reduction

For improving FCC gasoline quality, RIPP has also developed catalysts and promoters to reduce the sulfur content in FCC gasoline based on the activity of acid-catalyzed hydrogen transfer reactions and adsorption property [8,9]. Typical FCC gasoline contains mercaptans, thiophene, C1–C4-substituted thiophenes, thiophenols, C1 and C2 thiophenols, tetrahydrothiophene, and benzothiophene. Thiophenic compounds account for approximately 80% of total sulfur content. Due to their "aromatic" character, they are relatively stable in the FCC process. Therefore, the cracking of –C–S– bond in thiophene ring is an important reaction step in gasoline sulfur reduction under FCC condition. Different zeolites used as catalysts for the cracking-desulfurization of thiophene in the presence of different type of hydrocarbons have been investigated. The cracking-desulfurization of thiophene in *n*-octane over HY, Hβ and HZSM-5 zeolites has been tested. When *n*-octane conversion is 50%, thiophene conversion over HY, Hβ and HZSM-5 zeolites is 69, 47 and 43% and the corresponding sulfur content in liquid products is 2260, 4110 and 4300 μg/g, respectively. The activity for cracking-desulfurization reaction decreases in the following order: HY, Hβ and HZSM-5 zeolites. As for the acidic properties of zeolites, the acid site density of HY, Hβ and HZSM-5 zeolites measured by means of NH_3-TPD is 3.90, 2.75 and 1.99 μmol/m^2, respectively. The HY zeolite with higher acid site density favors the hydrogen transfer reaction. The structural pore diameter of HY, Hβ and HZSM-5 is 0.74, 0.70 and 0.54 nm, respectively. HY has a supercage with a diameter of 1.3 nm, which also promotes bi-molecular hydrogen transfer reaction. Hence, HY zeolite displays the highest activity for cracking-desulfurization among the tested zeolites. The bi-molecular hydrogen transfer reaction between hydrocarbon and thiophene is the prerequisite for the cracking-desulfurization of thiophene. The conversion of sulfur in different hydrocarbons tested increases in the following order: *iso*-octane, *n*-octane, and cyclohexane. Among the tested hydrocarbons, cyclohexane is the best one for cracking-desulfurization of thiophene. Obviously, cycloparaffin is an excellent hydrogen donor in hydrogen transfer reaction,

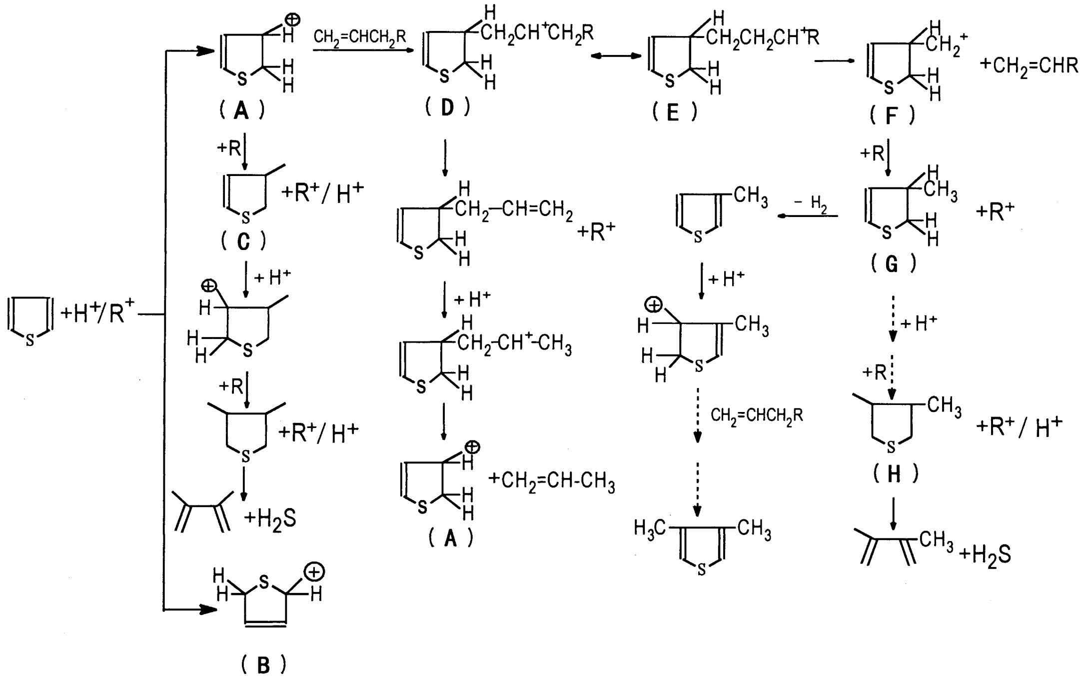

Fig. 5. A proposed mechanism for the cracking-desulfurization of thiophene in FCC process.

by transforming its structure into aromatics as many as six hydrogen atoms can be released. The reaction intermediates were determined by varying space velocity in a wide range. It was proved that tetrahydrothiophene is the key reaction intermediate in the cracking-desulfurization of thiophene. A mechanism has been proposed for thiophene cracking in FCC process, as shown in Fig. 5. The protonated thiophene species can react with either paraffins or olefins resulting in different reaction pathways. However, the ring saturation by hydrogen transfer is the prerequisite for the final C–S bonding cracking. A promoter catalyst has also been developed. The results of pilot test show that the sulfur content can be reduced by 20–30 wt.% after the addition of the promoter catalyst.

Acknowledgements

The project is under the auspices of the National Key Projects of Basic Research.

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