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CATALYTIC CRACKING OF VACUUM GAS OIL ON ALUMINA/ZEOLITES MIXTURES

– EFFECTS OF PRECIPITATION pH OF ALUMINA AND ZEOLITE TYPE ON PRODUCT DISTRIBUTION –

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Abstract – Catalytic cracking of vacuum gas oil on aluminas mixed with steam-treated zeolites (SY and SM) was investigated at 500 °C using a micro-activity tester. The catalysts containing SY and alumina prepared at pH 9.5 showed a higher conversion and more fraction of gasoline and K+D (kerosene+diesel) in products than those containing SM and alumina prepared at pH 7.8. This could be explained by acidic properties and pore structure of catalyst. The distribution of produced benzene, toluene and xylene on the catalyst containing SY or SM was different due to the pore size of zeolites. The difference in hydrogen transfer rate over the catalysts containing SY or SM leads to a different composition of unsaturated and saturated products.

Key words : Catalytic Cracking, Vacuum Gas Oil, Zeolite/Alumina, Zeolite Y and Mordenite, Ammonia TPD, Pore Structure

INTRODUCTION

Cracking catalyst allows a conversion of heavy oil into lower boiling fraction such as gasoline, kerosene and diesel. It is well known that the activity and the product distribution in catalytic cracking of hydrocarbon are affected by changes in both matrix and zeolite as a main component of catalyst [Campagna et al., 1992]. Since zeolite and matrix must be stable at high temperatures, zeolite is usually dealuminated by hydrothermal and chemical treatment [Biswas and Maxwell, 1990]. The role of zeolite in matrix is to extend the cracking degree for cracked hydrocarbon in mesopore of the matrix [Biswass and Maxwell, 1990].

Since the pore size of zeolite influences the product distribution significantly, considerable efforts have been made on the study of the different types of zeolites. In the case of modified zeolites Y and ZSM-5, product distribution obtained from the cracking of n-heptane was influenced by the pore size of zeolites [Corma et al., 1985]. The shape selectivity in various zeolites and silica-alumina for catalytic cracking of decalin isomers and naphthene has also been studied [Mostad et al., 1990]. The composition of bicycle products obtained by the cracking of long chain alkyl aromatics was significantly influenced by the pore size of the zeolite [Corma et al., 1994]. Among zeolites, mordenite with one-dimensional channel can be easily blocked around the pore mouth by coke formation in the cracking process of hydrocarbons [Guisnet and Magnoux, 1989; Mori et al., 1991]. Such coke formation is known to accelerate the deactivation of the reaction. The change of Bronsted and Lewis acid sites for H-mordenites due to the pretreatment at high temperatures was correlated with the composition of various product types such as alkane, alkene, aromatic and coke in the cracking of n-octane [Abbot and Guerzoni, 1992]. However, for vacuum gas oil containing various kinds of higher hydrocarbons such as polyaromatics, naphthenes and alkanes, there are not many studies relating to the difference in product distribution resulting from the zeolite type and precipitation pH of alumina. Therefore, in this study, we have investigated the product distribution for cracking reaction of vacuum gas oil by catalysts containing steam-treated zeolite Y (SY) or mordenite (SM) with different pore structure and silica/alumina ratio. Especially, the differences in product distribution of paraffin (P), olefin (O) and aromatic (A) in gasoline, and the selectivity of benzene (B), toluene (T) and xylene (X) in aromatics were discussed on the basis of zeolite type, acidic properties and pore structure of catalysts.

EXPERIMENTAL

1. Preparation of Catalysts

Na type mordenite (granule type of Norton Zeolon 900) and Na type zeolite Y (Linde LZY 52) were used as starting materials. These were treated with 1 M ammonium chloride solution at 80 °C, washed with distilled water, dried at 120 °C overnight and calcined at 500 °C for 5 hours to prepare H type zeolites. H type zeolites were then treated with 100 % steam for 3 hours and then calcined at 500 °C for 5 hours. H type mordenite and H type zeolite Y exposed to steam were designated as SM (SiO_2/Al_2O_3=6.5) and SY (SiO_2/

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Al_2O_3=3.0), respectively.

SM and SY as prepared were crushed to smaller than 200 mesh and dried at 300 °C for 12 hours under vacuum. The dried samples were impregnated completely with a 50 : 50 mixture of n-hexane and iso-hexane before they were mixed with an aluminum nitrate solution to prevent precipitating aluminum hydroxide in the pore of zeolites. The impregnated zeolites with hexane mixture were then added into an aluminum nitrate solution so that zeolite content became 35 wt% based on the total weight of the formed zeolite/alumina. Aluminum hydroxide was precipitated as a result of the reaction of aluminum nitrate with ammonia in water and pHs of solutions were kept at 7.8 or 9.5 during precipitation. The precipitated aluminum hydroxide was aged for 20 hours at room temperature. Precipitated aluminum hydroxide with SY (or SM) was then filtered, dried at 120 °C overnight and then calcined at 600 °C for 3 hours under air stream to form γ-alumina. These samples were designated as SM/A (7.8 or 9.5), and SY/A (7.8 or 9.5), in which A denotes alumina, and 7.8 and 9.5 in parenthesis represent the pH values during precipitation.

2. Characterization of Catalysts

All samples were pretreated in vacuum at 300 °C for 6 hours for the characterization of adsorption. The adsorption/desorption isotherms of nitrogen on the zeolites and zeolite/aluminas were obtained at liquid nitrogen temperature using a Micromeritics ASAP-2000. From the isotherms, the specific surface area using BET adsorption equation and pore volume were determined.

Acidity of samples was determined by temperature programmed desorption (TPD) of ammonia (Altamira Co. AMI-1) equipped with a thermal conductivity detector. Samples of 0.3 gram with 100-200 mesh size were evacuated in a quartz cell at 500 °C for 1 hour and ammonia gas was admitted to adsorb on the samples at 100 °C for 30 min and then dried at the same temperature for 1 hour under helium stream. The temperature for ammonia-TPD was linearly raised up to 900 °C at a heating rate of 10 °C/min. The spectra of ammonia-TPD were obtained under helium flow, 30 cc/min. The coke formed during the reaction was analyzed by elemental analyzer (Heraeus Co., vario EL), in which the burning temperature was 1,200 °C by passing oxygen through sample (about 3 mg). The evolved gases such as carbon dioxide, sulfide dioxide and water from coke on catalyst were detected by GC with TCD.

3. Reaction Procedure and Analysis

The catalytic activity was measured at 500 °C in a modified micro-activity tester (MAT) based on ASTM D-3907-87 [Lee and Ha, 1996]. Catalyst of 1.7 g was loaded in the micro-reactor, and vacuum gas oil (VGO) having average molecular weight ranging from 360 to 380 (Table 1) was injected into the reactor within 75 seconds to make the catalyst-to-oil ratio be 2.0 (g catalyst/g oil). During the reaction, liquid products were collected in a cooled reservoir by ice. Gaseous products were trapped by water displacement. At the end of reaction, the reactor was purged with nitrogen for 20 min. The purged gases were also collected for analysis.

Trapped liquid product was analyzed by gas chromatography with a capillary column and FID detector. Each peak of the products in the range of gasoline was identified with mass spectrum analyzer. The products in the gasoline were classified to paraffin (P), olefin (O), naphthene (N) and aromatic (A), and their fractions were defined as the percentage of each component. The gasoline, kerosene+diesel (K+D) and vacuum gas oil were fractionated by HT-SIMDIST with a capillary column coated by metal silicon. The fractions of gasoline and K+D were defined as the percentage of each component in the liquid products excluding gas and coke.

Table 1. Characterization data for vacuum gas oil of SK Corporation

Description	VGO
Elemental analysis	
C (wt%)	85.77
H (wt%)	13.01
N (wt%)	0.53
Molecular weight	
Number average (N)	356
Weight average (W)	365
Viscosity average (V)	365
API	23.1
Conradson carbon (%)	0.2
Distillation distribution (vol%, °C)	
IBP	287
5	342
10	362
50	440
90	508
95	523
EP	545
Average composition of reaction material (vol%)[a]	
Saturate	66
Aromatic	33
Polar	1

[a]: HPLC analysis

RESULTS AND DISCUSSION

1. Characterization of Catalysts

The specific surface areas, pore volumes of zeolites (SM and SY) of zeolite/aluminas (SM/A (7.8 or 9.5) and SY/A (7.8 or 9.5)) obtained from the nitrogen isotherm are shown in Table 2, including the volume ratio of mesopore to micropore for these catalysts. It can be seen from the specific surface area and the pore volume that pure zeolites have mostly the micropore, and SY in pure zeolites has better pore structure compared to that of SM. However, zeolite/aluminas have high ratio of mesopore volume to total volume due to the mesopore of alumina. Among zeolite/aluminas, the catalysts containing SY or prepared at pH 9.5 have larger mesopore volume than those containing SM or prepared at pH 7.8. This suggests that zeolite/aluminas containing larger volume of mesopore are expected to be better catalysts, because of the easy diffusion of large molecular reactants within pore.

Fig. 1 shows the TPD spectra of ammonia on alumina (pH 9.5), pure zeolites and zeolite/aluminas. All samples have two desorption peaks at about 230 °C and 650 °C. The acid a-

Table 2. Surface areas and pore volumes over zeolites and zeolite/aluminas

Catalyst	Surface area (m^2/g)			Pore volume (cc/g)			Mesopore/Micropore volume
	BET	Micro-	External	Total	Micro-	Meso	
SM	500	485	15	0.217	0.186	0.031	0.16
SY	822	735	87	0.397	0.283	0.111	0.39
SM/A (7.8)	323	118	205	0.294	0.053	0.242	4.59
SM/A (9.5)	319	108	211	0.312	0.048	0.264	5.46
SY/A (7.8)	345	117	228	0.346	0.052	0.293	5.60
SY/A (9.5)	353	73	280	0.412	0.033	0.378	11.32

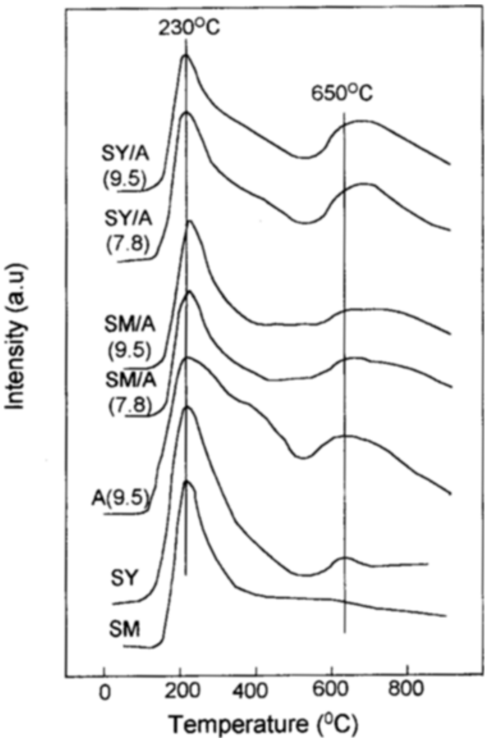

Fig. 1. Ammonia-TPD profiles over alumina (A), zeolites (SM, SY) and zeolite/aluminas (SM/A, SY/A).

mount of the catalyst containing SY with high acid site density is larger than that of the catalyst containing SM. A desorption peak at 650 °C in pure zeolites is remarkably small compared to the peak at 230 °C. However, the desorption peak at 650 °C was observed to be enlarged in zeolite/aluminas due to strong acid sites which appeared on alumina (pH 9.5). Among zeolite/aluminas, the catalysts containing SY have a larger number of strong acid sites than the catalysts containing SM.

2. Activity and Product Distribution

The conversion of reactants and the amount of coke formed by pure zeolites and zeolite/aluminas in the process of the cracking of VGO are shown in Table 3. Overall liquid products obtained by the catalysts containing SM(A) or SY (B) were analyzed by HT-SIMDIST instrument and are shown as the spectra in Fig. 2. The liquid product is fractionated into gasoline, kerosene+diesel (K+D) and VGO on the basis of HT-SIMDIST spectra for commercial oil produced from SK Corp. The fractions of gasoline and K+D in liquid products are presented in Table 3. It shows that the catalysts containing SY were more active and yielded more gasoline and K+D than those containing SM. This can be explained by tak-

Table 3. Conversion, fraction of gasoline and kerosene+diesel, and coke amount obtained from the cracking of vacuum gas oil on zeolites and zeolite/aluminas LWHSV 24 hr^{-1}

Catalyst	Conversion (%)	Fraction in liquid product		Coke amount (g/g-cat.)
		Gasoline	K+D	
SM	37.1	15.8	2.8	3.85
SM/A (7.8)	30.0	16.2	5.9	2.93
SM/A (9.5)	39.2	18.2	9.3	2.13
SY	80.2	50.7	25.3	6.12
SY/A (7.8)	62.9	44.0	29.6	4.24
SY/A (9.5)	80.3	51.7	28.0	5.01

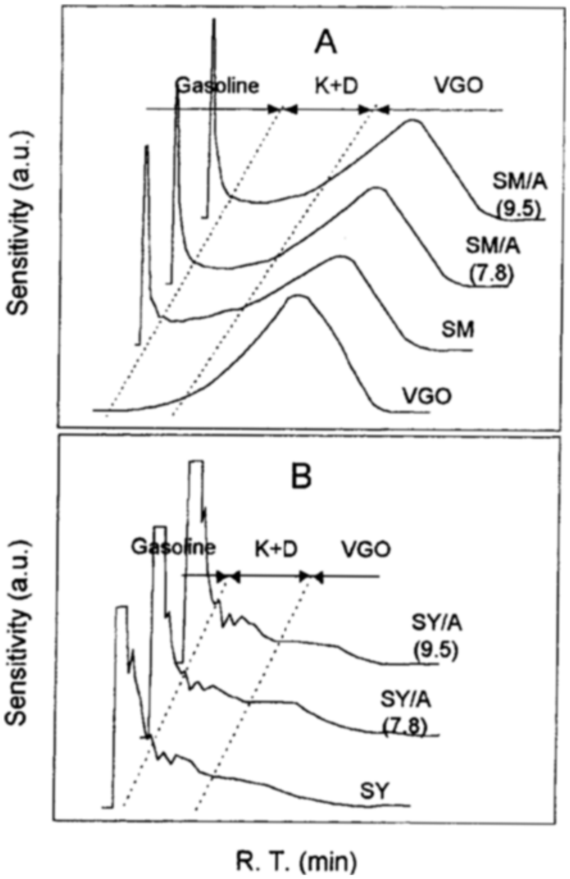

Fig. 2. HT-SIMDIST spectra of products obtained from cracking reaction of VGO on SM, SM/A (A) and SY, SY/A (B). LWHSV : 24 hr^{-1}, reaction temperature : 500 °C.

ing into account the acidic site density and pore structure of zeolites. That is, high acid site density and three dimensional channel in zeolite Y are preferred for the activity and selectivity of gasoline and K+D compared to the low acidic site density and one dimensional channel of mordenite. Accordingly, the accessibility of the reactant in zeolite Y of large kinetic diameter is better than the mordenite so that large molecular reactant can be broken easily at the active sites within the mesopore. The catalysts containing zeolite produced a greater yield of gasoline than that of K+D, which implies that the zeolite is an active component for obtaining the gasoline mainly.

In comparison of pure zeolites with zeolite/aluminas, the conversion of VGO on zeolite is almost the same as that of zeolite/aluminas. This means that zeolite/aluminas are actually more active than the pure zeolite because only 35 % zeolite plays a major role in the cracking activity. Zeolite/aluminas have yielded more K+D than pure zeolites. This could be attributed to the easy diffusion of the initially cracked products at active sites on mesopores of alumina. Among the aluminas mixed with zeolite, the catalysts prepared at pH 9.5 show a higher conversion than those at pH 7.8 because the zeolite/aluminas prepared at pH 9.5 have larger mesopore volume as shown in Fig. 1. Alumina precipitated at pH 7.8 has an unimodal pore structure having a pore diameter of around 4 nm. On the contrary, the one precipitated at pH 9.5 has a bimodal pore structure having a pore diameter of around 4 and 7 nm [Lee and Ha, 1996]. Previous work [Huang et al., 1989] showed that at below pH 9 a pseudoboehmite of an unimodal pore structure was formed, but at above pH 9 both pseudoboehmite and bayerite could be formed resulting in bimodal pore structures. Therefore, the result can be explained as follows: the development of mesopore structure would make better accessibility of the bigger reactants to zeolite active sites.

The coke amount formed during the cracking of VGO on various catalysts is shown in Table 3. Pure zeolites can retain more coke compared to zeolite/aluminas because coke molecules could easily penetrate into the micropores of zeolite [Dimon et al., 1993]. In different type of zeolites, a high density of aluminum atoms requires a high hydrogen transfer rate through inductive effects [Corma et al., 1990]. Accordingly, SY having high acid site density compared to SM produced more coke by means of intermolecular hydrogen transfer reaction between adsorbed alkylaromatic species.

The fractions of saturated paraffin (P), unsaturated olefin (O) and aromatics (A) in gasoline products are presented in Fig. 3. The catalysts containing SY produced more saturated paraffins than those containing SM. Since SY has a higher acid site density than SM, this result might be due to the fast hydrogen transfer rate between two adjacent active sites of SY by means of bimolecular Eley-Rideal mechanism [Biswas and Maxwell, 1990]. Therefore, a higher hydrogen transfer rate leads to more paraffin formation and less olefin formation. Considering the influence of shape selectivity on product distribution, SY having a pore structure of large kinetic diameter has yielded more aromatics than SM. The product distributions of benzene, toluene and xylene in aromatics on catalysts containing SY or SM are shown in Fig. 4. The highest fraction of xylene was obtained over the catalyst containing SY, whereas the catalyst containing SM yielded the highest fraction of toluene. Also the catalysts containing SY produced relatively more toluene and xylene, but less benzene compared to the catalysts containing SM. The difference of product distribution can be explained by the influence of pore size in zeolites [Guerzoni and Abbot, 1994].

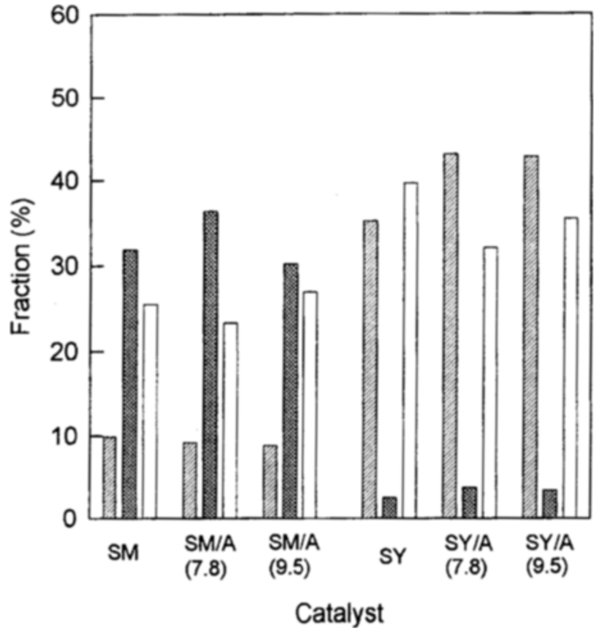

Fig. 3. The fraction of paraffin (▨), olefin(▩) and aromatic (☐) in the gasoline obtained from cracking of VGO on zeolites and zeolite/aluminas with LWHSV 24 hr^{-1}.

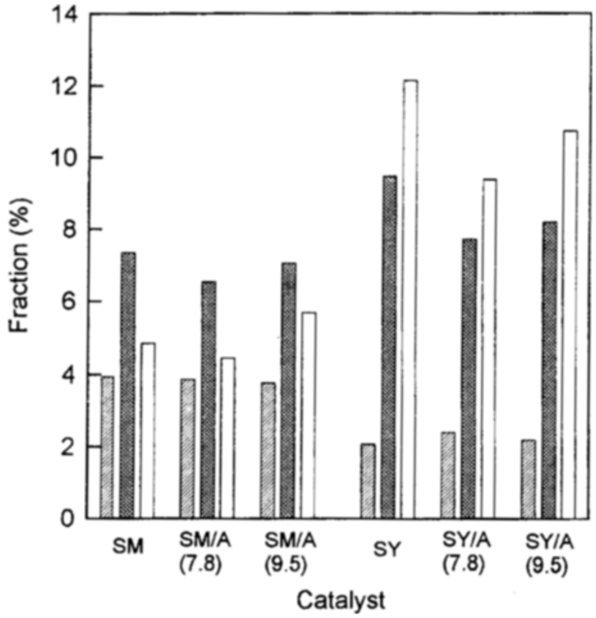

Fig. 4. The fraction of benzene (▨), toluene (▩) and xylene (☐) in the aromatic obtained from cracking of VGO on zeolites and zeolite/aluminas with LWHSV 24 hr^{-1}.

CONCLUSIONS

The activity and product distribution obtained from catalytic cracking of vacuum gas oil have been investigated over alumina (precipitated at pH 7.8 and 9.5) mixed with zeolite Y (SY) or mordenite (SM).

The catalysts containing SY prepared at pH 9.5 showed a higher conversion and more fraction of gasoline than those containing SM prepared at pH 7.8. This could be explained by taking into account the high acidic site density of zeolite and pore structure of catalyst. The catalysts containing SY of high acidic site density yielded more paraffin and coke, and less olefin than those containing SM. This is attributed to an intermolecular hydrogen transfer reaction at two adjacent active sites.

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