

## THE INFLUENCE OF MORDENITE CHARACTERISTICS IN MORDENITE MIXED WITH ALUMINA ON CRACKING OF VACUUM GAS OIL

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**Abstract**—Catalytic cracking of vacuum gas oil has been investigated at 500 °C over mixed catalysts in a micro-activity tester. The catalyst consists of mordenite treated by either HCl/steam or HF and alumina prepared at pH of 9.5 or 7.8. The catalysts retaining mordenite in which SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> weight ratio ranged from 15 to 20 show the maximum activity and selectivity for gasoline. Both the activity and selectivity for gasoline seem to depend strongly on both acid strength of mixed catalysts and mesopore volume of the mordenite. It is found, however, that the selectivity of kerosene+diesel in liquid product as well as the yield of aromatics in gasoline are influenced more by mesopore volume of mordenite than by acid properties of mordenite in the catalyst of mordenite/alumina.

*Key words:* Catalytic Cracking, Vacuum Gas Oil, Pretreatment, Mordenite/Alumina, Mesopore of Mordenite

### INTRODUCTION

Cracking catalysts have been used to obtain a high proportion of gasoline product from heavy reactants. Commercial fluid cracking catalysts consist of zeolite as a main component and silica-alumina as a matrix. Since both zeolite and matrix must be stable at high temperature, zeolite may be modified by steam or acid treatment in order to dealuminate. Among zeolites, mordenite has high thermal stability but low accessibility of large molecular weight reactants in micropore of mordenite with one dimensional channel [Breck, 1974]. Therefore, it is needed to modify mordenite by extracting aluminum species from the lattice without deteriorating extensively the crystallinity of the matrix [Lee et al., 1997]. Dealumination of mordenite leads to form mesopores and results in the formation of mild acid properties.

A number of investigation indicated the importance of catalyst pore size and pore size distribution in cracking of large molecular weight hydrocarbons. Corma and coworkers [Corma et al., 1994] investigated the cracking of hydrocarbons on zeolites with different pore sizes, and the cracking of 1-phenylheptane over zeolite Y, beta, mordenite, ZSM-5 and silica-alumina. They reported that bicyclic products were influenced by pore size of zeolite. Also the product distribution in gasoline range obtained from the cracking reaction of heavy

oil containing a high proportion of linear paraffins was distinctly different on HY and ZSM-5 [Guerzoni and Abbot, 1994]. The change of physico-chemical properties of mordenite used as a cracking catalyst results in different activities and selectivities of products such as gasoline and kerosene+diesel in liquid product as well as olefin, aromatic and branched aromatics in gasoline range [Lee et al., 1997]. Song et al. studied that the effect of catalyst pore structure of Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts on asphaltene conversion and found that the performance of the catalysts strongly depend on their pore structure [Song et al., 1991].

In this study, mordenite in mordenite/alumina mixed catalyst was treated by either HCl/steam or HF in order to obtain the mesopores for easy diffusion of large reactant and to change the acid properties. The effect of the characteristics of modified mordenite such as pore size, acid strength and different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> weight ratio on the cracking activity of VGO and the selectivities of the products such as gasoline, kerosene+diesel, aromatic, olefin and branched aromatics will be investigated.

### EXPERIMENTAL

#### 1. Preparation of Catalysts

Na type mordenite (granule type of Norton Zeolon 900) as a starting mordenite was treated with 1 N ammonium chloride solution at 80 °C for ion-exchange. The NH<sub>4</sub> type mordenite was washed with distilled water, dried at 120 °C overnight and calcined at 500 °C for 5 hours to prepare H type mordenite. The H type mordenite was then treated with 100 % steam for 3 hours followed by calcining at 500 °C for the

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same hours. The H type mordenites exposed to steam are denoted as SM<sub>6.5</sub> (subscript 6.5 indicates weight ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=6.5). In order to construct the secondary pores of SM<sub>6.5</sub>, extraction of aluminum oxide from mordenite was accomplished by treatment with 6 N HCl at 90°C for 4 hours, 6 hours, or 21 hours and followed by steaming at 500°C for 3 hours, 6 hours, or 10 hours. Such dealuminated mordenites were then treated with 0.01 N HCl at 90°C for 2 hours to remove extra-framework aluminum from the pore mouth. These catalysts were classified as SM<sub>15.5</sub>, SM<sub>20</sub>, or SM<sub>39</sub>, respectively, in which subscripts indicate SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> weight ratio. To prepare FM series catalysts, SM<sub>6.5</sub> was further dealuminated by treatment of 0.5 N HF solution at room temperature for 192 hours, 240 hours, 384 hours, or 528 hours, respectively, and these samples were abbreviated by FM<sub>17</sub>, FM<sub>17.5</sub>, FM<sub>21</sub> and FM<sub>21.5</sub>, respectively. Each dealuminated mordenite was finally treated by steam at 500°C for 3 hours in order to remove HCl or HF bonded weakly on external surface of mordenite and followed by calcining at 500°C for 3 hours.

Dealuminated mordenites were crushed to sizes smaller than 200 mesh and dried at 300°C for 12 hours under vacuum. The dried samples were saturated completely with a 50:50 mixture of n-hexane and iso-hexane before they were mixed with aluminum nitrate solution to prevent precipitation of aluminum hydroxide in the pores of mordenites. The saturated mordenites with hexane mixture were then added into aluminum nitrate solution in such a way that mordenite content is 35 wt % based on the formed mordenite/alumina. Aluminum hydroxide was precipitated as a result of the reaction of aluminum nitrate with ammonia water in which pH is controlled at either 7.8 or 9.5. The precipitated aluminum hydroxide was aged for 20 hours at room temperature. Precipitated aluminum hydroxide with mordenite was then filtered, dried at 120°C overnight and then calcined at 600°C for 3 hours under air stream to form  $\gamma$ -alumina. These samples were denoted as SM<sub>X</sub>/A (7.8 or 9.5) and FM<sub>X</sub>/A (7.8 or 9.5), in which subscript X and A indicate SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> weight ratio and alumina, and 7.8 and 9.5 in parenthesis represent the pH value during precipitation.

The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> weight ratio of dealuminated mordenites was determined by X-ray fluorescence (Philip, PW-1480). The samples were mixed with a flux of dilithium tetraborate and measured by fusion at 1,000-1,200°C. 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 mordenite/alumina were obtained at liquid nitrogen temperature using Micromeritics ASAP-2000. From nitrogen desorption branches of the isotherms, the pore size distributions were obtained by BJH method. Infrared spectra of samples pressed into thin wafers (9 mg/cm<sup>2</sup>) and outgassed overnight at 400°C in vacuum ( $3 \times 10^{-3}$  mmHg) were measured using Magma-IR spectrometer (Nicolet Co.). Pyridine was admitted into the IR cell at room temperature and the samples were equilibrated at 150°C, 250°C and 350°C, respectively, for 1 hour in vacuum ( $3 \times 10^{-3}$  mmHg) prior to measuring the spectra with arbitrary unit in the region of 2,000-1,300 cm<sup>-1</sup>.

## 2. Reaction Procedure

The catalytic activity was measured in a modified micro-

activity tester (MAT) according to ASTM D-3907-87. Catalyst of 1.7 g was loaded in the micro-reactor and pretreated with nitrogen for 30 min at 500°C. Average molecular weight of the vacuum gas oil (VGO) used in this study as a reactant ranged from 360 to 380. The VGO (0.9 ml) was injected into the reactor within 75 s to have the catalyst-to-oil ratio of 2 (g catalyst/g oil). During the reaction, liquid products were collected in a cold trap. Gaseous products were trapped by means of water displacement. At the end of run, the reactor was purged with nitrogen for 20 min and the purged gaseous products were also collected for analysis. Trapped liquid products were analyzed by a gas chromatograph (Shimadzu, GC-14A) with a capillary column (CBP-1, 25 m  $\times$  0.25  $\mu$ m) and an FID detector. Each peak of the products in the range of gasoline was identified with a mass spectrometer (Shimadzu, GCMS-QP5000). The products in the gasoline range were classified to paraffin (P), olefin (O), naphthene (N) and aromatic (A), and their fractions were defined as the weight percentage of each component. The gasoline, kerosene+diesel (K+D) and vacuum gas oil were fractionated by HT-SIMDIST (Fisons) with a capillary column (7 m  $\times$  0.58 mm) coated by metal silicon. The fractions of gasoline and K+D were defined as the weight percentage of each component in the liquid products excluding gas and coke.

## RESULTS AND DISCUSSION

### 1. Activity

Fig. 1 shows the conversion of VGO on the catalysts which

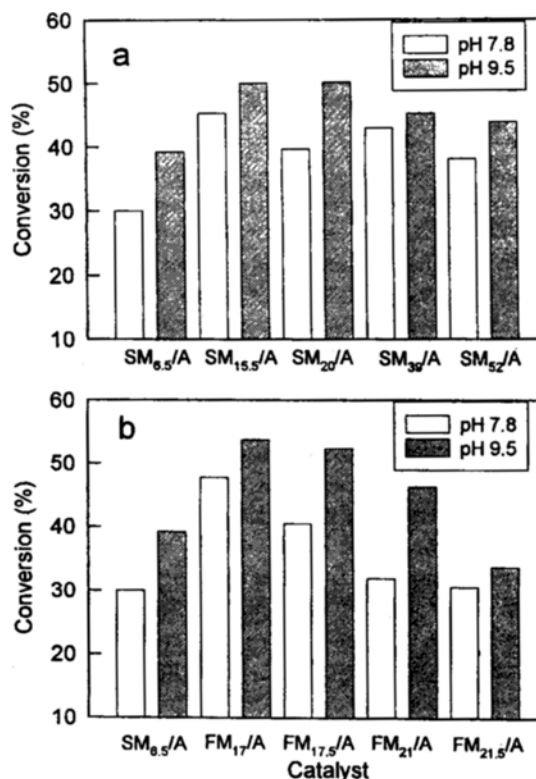


Fig. 1. Conversion obtained from catalytic cracking of vacuum gas oil on alumina mixed with mordenite treated by HCl/steam (a) and HF (b), respectively.

consist of mordenite treated by either HCl/steam (SMs) or HF (FMs) and the alumina prepared at pH of 7.8 or 9.5. The conversion of VGO on the catalyst in which alumina was prepared at pH 9.5 is higher than that at pH 7.8. This is attributed to the larger pore size and broader mesopore size distribution shown in Fig. 2 as well as higher acid strength shown in Table 1. The highest conversion is obtained on the mixed catalysts in which mordenite has SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> weight ratio ranged from 15 to 20 regardless of the dealumination methods. This result is consistent with the cracking of VGO over a pure mordenite [Lee, 1996]. The increase in conversion from 30 % of SM<sub>6.5</sub>/A (pH 7.8) to 53 % of FM<sub>17</sub>/A (pH 9.5) can be explained by the fact that the formation of mesopore makes large size reactant diffuse easily and the acid strengths become magnified even though acid amount is reduced during dealumination process. Therefore, the catalytic performance in the mixed catalyst used in this study is influenced by the physico-chemical characteristics of mordenite and pore size distribution of alumina.

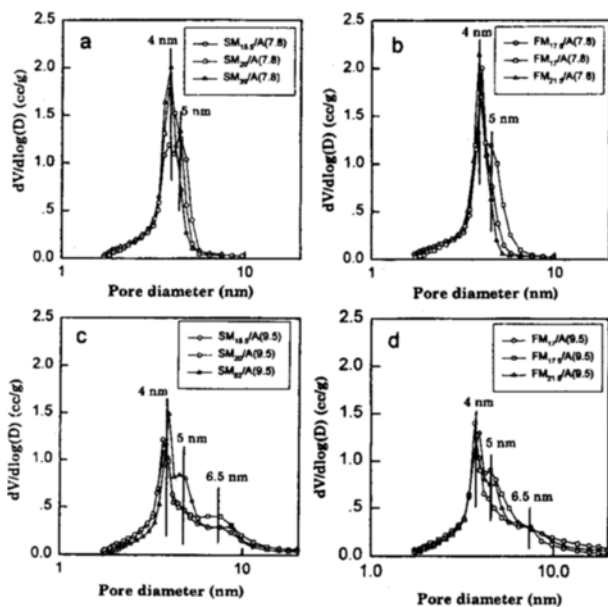


Fig. 2. Pore size distributions obtained by nitrogen desorption isotherm branches over the mixed catalysts.

## 2. Selectivities of Gasoline and Kerosene+Diesel in Liquid Product

The fractions of gasoline and kerosene+dieasel (K+D) obtained from the liquid product of VGO cracking on SM/As and FM/As are shown in Fig. 3 and Fig. 4. The gasoline fraction shows similar trend with the conversion of VGO. The gasoline fraction is increased as the cracking activity is increased up to 60 % of conversion. In other words, the gasoline yield becomes high on the mixed catalyst where mordenite has the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 15 to 20 and alumina is prepared at pH 9.5. Therefore, optimum design of mixed catalyst depends not only on the precise control of mordenite

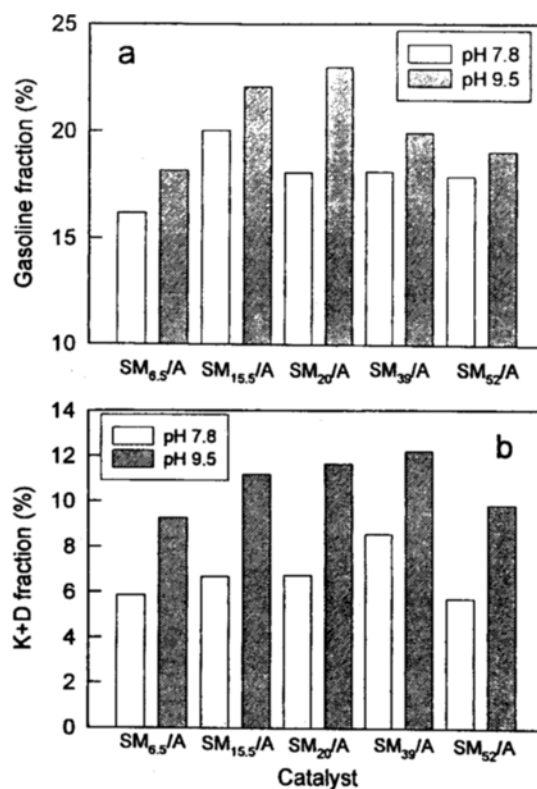


Fig. 3. Fractions of gasoline (a) and kerosene+dieasel (b) in liquid product obtained from catalytic cracking of vacuum gas oil on alumina mixed with mordenite treated by HCl/steam.

Table 1. The acid site type and acid strength distributions in mordenite mixed with alumina measured by IR-pyridine adsorption

Catalyst	Brönsted acid sites (a.u.) <sup>a</sup>			Lewis acid sites (a.u.) <sup>a</sup>			Acid strength (B+D)/(A+C)
	150 °C (A)	250 °C	350 °C (B)	150 °C (C)	250 °C	350 °C (D)	
SM <sub>6.5</sub> /A (7.8)	0.9	0.7	0.5	11.6	4.4	3.0	0.28
SM <sub>15.5</sub> /A (7.8)	0.1	0.1	0.1	9.3	5.5	2.6	0.29
SM <sub>39</sub> /A (7.8)	0.25	0.2	0.2	11.2	5.1	1.7	0.17
SM <sub>6.5</sub> /A (9.5)	1.0	1.0	0.7	11.6	6.4	5.0	0.45
SM <sub>15.5</sub> /A (9.5)	0.25	0.2	0.2	9.7	4.4	3.2	0.34
SM <sub>39</sub> /A (9.5)	0.3	0.2	0.2	8.9	5.5	3.0	0.35
FM <sub>17.5</sub> /A (7.8)	0.9	0.8	0.5	8.3	5.2	3.3	0.41
FM <sub>21.5</sub> /A (7.8)	0.25	0.3	0.2	9.8	4.9	2.5	0.26
FM <sub>17.5</sub> /A (9.5)	1.0	1.0	0.6	8.9	4.5	4.3	0.49
FM <sub>21.5</sub> /A (9.5)	0.45	0.5	0.4	8.6	5.1	3.5	0.43

<sup>a</sup>Values of intensity calculated for 9 mg/cm<sup>-2</sup> samples at the specified temperatures (°C).

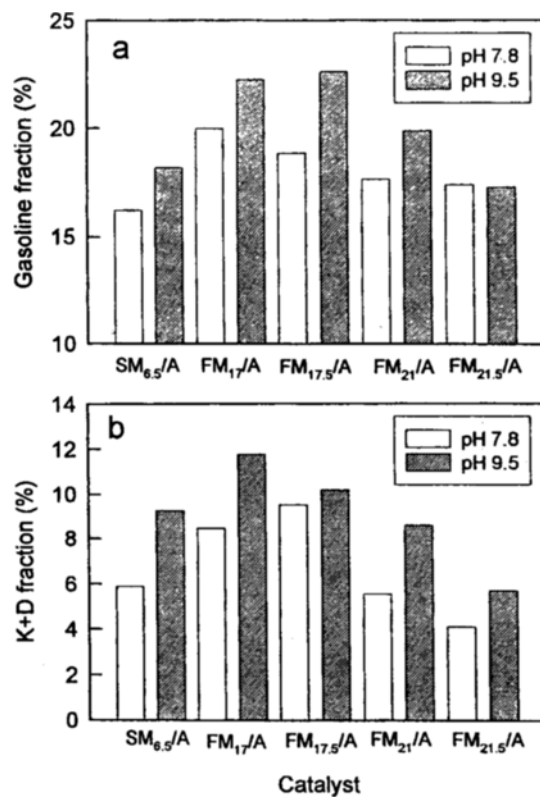


Fig. 4. Fractions of gasoline (a) and kerosene+diesel (b) in liquid product obtained from catalytic cracking of vacuum gas oil on alumina mixed with mordenite treated by HF.

properties but also on the proper preparation of alumina. It is of importance that appropriate control of pore size distribution and acid properties should be accomplished so that large molecules like VGO can be cracked first on the active site of alumina with mesopore and subsequent cracking can occur on the active site of mordenite with micropore.

The fraction of K+D shows high yield on the mixed catalyst prepared at pH=9.5 in which mesopore size distribution is broad as shown in Fig. 3b and Fig. 4b. It can be also seen that the highest yield of K+D is obtained over SM<sub>39</sub>/A among HCl/steam-treated catalysts and over FM<sub>17</sub>/A among HF-treated catalysts. In the case of pure mordenite, the highest yield of K+D is obtained over the catalyst where the mesopore volume is maximum although acid amount and acid strength is rather low due to severe dealumination [Lee, 1996]. These results lead to the conclusion that the selectivity of large molecules like kerosene and diesel is influenced by mesopore size distribution rather than acid properties.

### 3. Selectivities of Aromatic, Olefin and Branched Aromatic in Gasoline

Fig. 5 and Fig. 6 show the fractions of aromatics and olefins in the gasoline product obtained from VGO cracking over FM/As and SM/As. The aromatic yield over the catalysts in which alumina was prepared at pH=9.5 is higher than those at pH=7.8 as shown in Fig. 5a and Fig. 6a, because the catalysts prepared at pH=9.5 had larger mesopore size and broader bimodal mesopore size distribution than those prepared at

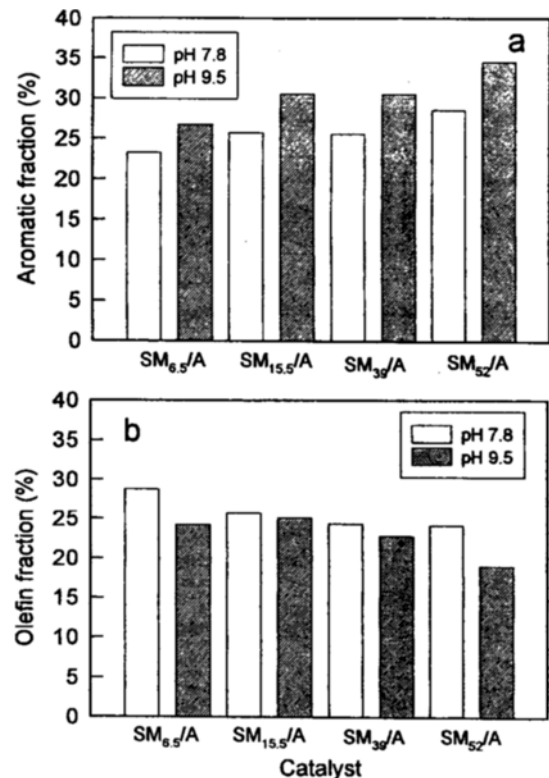


Fig. 5. Fractions of aromatic (a) and olefin (b) in the gasoline obtained from catalytic cracking of vacuum gas oil on alumina mixed with mordenite treated by HCl/steam.

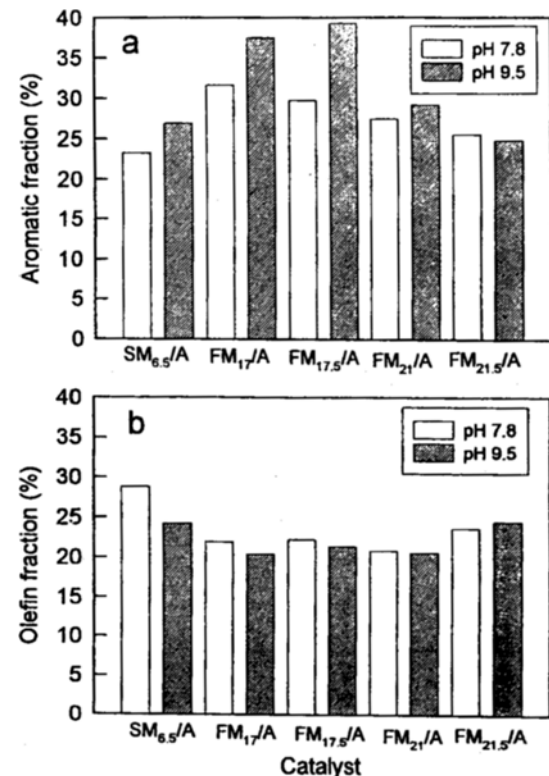


Fig. 6. Fractions of gasoline (a) and kerosene+diesel (b) in liquid product obtained from catalytic cracking of vacuum gas oil on alumina mixed with mordenite treated by HF.

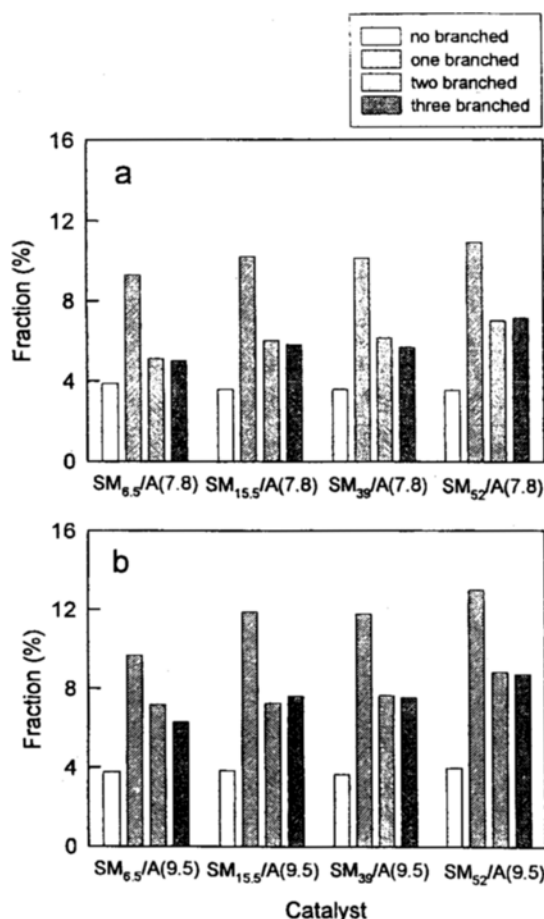


Fig. 7. Fraction of branched aromatic in the gasoline obtained from catalytic cracking of vacuum gas oil on alumina mixed at pH=7.8 (a) and pH=9.5 (b) with mordenite treated by HCl/steam.

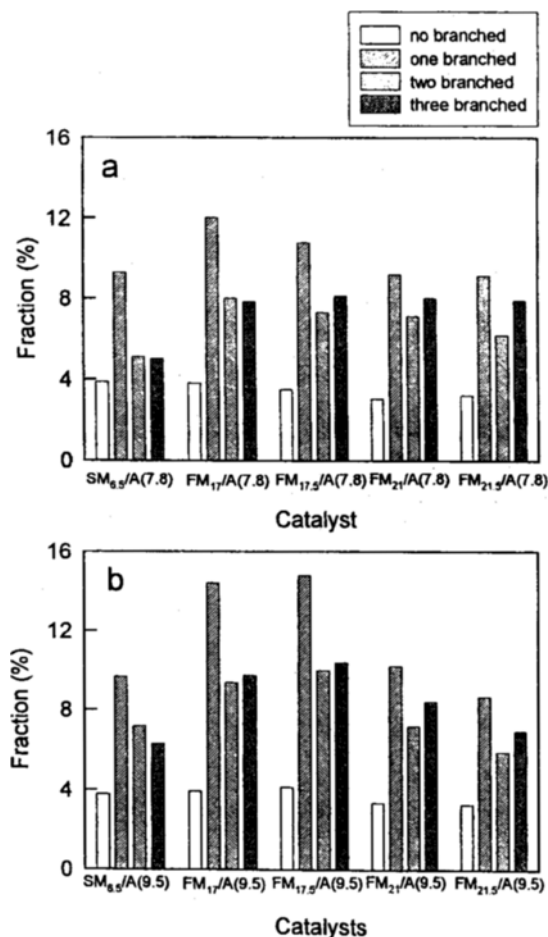


Fig. 8. Fraction of branched aromatic in the gasoline obtained from catalytic cracking of vacuum gas oil on alumina mixed at pH=7.8 (a) and pH=9.5 (b) with mordenite treated by HF.

pH=7.8 shown in Fig. 2. In two series of FM/As and SM/As, the catalysts of SM<sub>52</sub>/A and FM<sub>17.5</sub>/A containing SM<sub>52</sub> and FM<sub>17.5</sub> in which mesopore is well developed have the highest fraction of aromatics [Lee et al., 1997].

Both the fraction of olefin shown in Fig. 5b and Fig. 6b and the fraction of aromatic shown in Fig. 5a and Fig. 6a shows reverse relationship. It can be explained that low molecular weight olefins are converted to aromatics via oligomerization followed by aromatization and high molecular weight olefins are converted to aromatics via direct aromatization [Lee et al., 1997].

The fractions of branched aromatics in the gasoline product obtained from catalytic cracking of VGO over SM/As and FM/As are shown in Fig. 7 and Fig. 8. The fraction of branched aromatics, as a function of pH and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of mordenite in the catalyst, has similar tendency with the fraction of aromatic shown in Fig. 5a and Fig. 6a. That is, the catalysts prepared at pH 9.5 which have large mesopore size and broad bimodal mesopore size distribution, and the catalysts containing mordenites in which mesopore is well developed have higher fraction of branched aromatics due to higher fraction of aromatic. It is also seen that, as a function of catalyst mixed with mordenite of different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>

weight ratio, the fraction of benzene in aromatic products is almost constant over all catalysts whereas the fraction of branched aromatic is increased over the catalysts containing dealuminated mordenite in which mesopore was developed gradually with increase of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> weight ratio, irrespective of acid properties, during severe dealumination process of mordenite. Especially the aromatic with one branch such as toluene and ethylbenzene is obtained as the major component among branched aromatics over all catalysts.

## CONCLUSION

Alumina mixed with mordenite which was treated by HCl/steam (SM) or HF (FM) has been studied for catalytic cracking of VGO at 500 °C.

The maximum conversion and selectivity of gasoline in liquid product were obtained over alumina mixed with mordenites which have the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> weight ratio of 15-20 regardless of the treatment method of mordenite. It can be explained by taking into account acid strength of mixed catalysts and mesopore volume of mordenite.

The selectivities of kerosene+diesel in liquid product and branched aromatics in gasoline product were high owing to

a high proportion of mesopore volume of mordenite included in mordenite/alumina, although mordenite has low acid amount and low acid strength by severe dealumination of mordenite.

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