Increasing Octane Value in Catalytic Cracking of \textit{n}-Hexadecane with Addition of *BEA Type Zeolite

Iori Shimada *, Ryoichi Imai, Yoshinori Hayasaki, Hiroshi Fukunaga, Nobuhide Takahashi and Toru Takatsuka

Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567 Japan; E-Mails: imai@nomjim.co.jp (R.I.); hayatyaki@gmail.com (Y.H.); fuku@shinshu-u.ac.jp (H.F.); novhide@shinshu-u.ac.jp (N.T.); t-tsuka@shinshu-u.ac.jp (T.T.)

* Author to whom correspondence should be addressed; E-Mail: iori@shinshu-u.ac.jp; Tel.: +81-268-21-5466 (ext. 5466); Fax: +81-268-21-5391.

Academic Editor: Russell R. Chianelli

Received: 26 December 2014 / Accepted: 14 April 2015 / Published: 22 April 2015


doi:10.3390/catal5020703

\textbf{Abstract:} In this study, multifunctional catalysts were developed by adding *BEA or MFI zeolite with high Si/Al ratio to a residual fluidized catalytic cracking (RFCC) catalyst and tested in the catalytic cracking of \textit{n}-hexadecane, which is a heavy crude oil model compound, for the purpose of increasing the octane value of produced gasoline under the strong hydrogen transfer activity of the RFCC catalyst. Reaction products analysis revealed that the addition of *BEA zeolite to the RFCC catalyst increased the yields of olefins and multi-branched paraffins, which resulted in improvement of the octane value without sacrificing gasoline yield. On the contrary, the addition of MFI zeolite decreased the gasoline yield because it cracks the gasoline range olefins into LPG range olefins. In general, it is difficult to increase the yield of multi-branched molecules because the multi-branched molecule is more easily cracked than linear molecules. Our results suggest the possibility for the selective acceleration of isomerization reaction by the addition of less acidic *BEA zeolite to the RFCC catalyst.

\textbf{Keywords:} RFCC process; hydrogen transfer; isomerization; *BEA zeolite; MFI zeolite; octane number
1. Introduction

To maintain a steady supply of gasoline, it is important to increase the refining capacity and expand the range of heavy oils able to be processed. Residue fluidized catalytic cracking (RFCC) catalyst can crack the heavy oils into valuable gasoline fractions [1], but the catalysts with higher bottom conversion activity also tend to accelerate the hydrogenation of olefins into paraffins simultaneously, which results in an octane loss.

An octane value is determined by the composition of the gasoline fraction constituent, and it obeys the order of aromatics ≈ naphthenes ≈ olefins > paraffins. Compared to the same type of compounds, a molecule with a smaller carbon number has a higher octane value. If the carbon number is the same, a multi-branched molecule has higher octane value than a linear molecule. In the RFCC process, olefins are converted into paraffins by the strong hydrogen transfer activity of the FAU zeolite contained in the RFCC catalyst. However, if the olefins can be converted from linear molecules into multi-branched molecules before the hydrogenation reaction, a high octane value will be maintained even after the hydrogenation reaction in the strong hydrogen transfer activity condition.

In a catalytic cracking process, several types of zeolites are used as catalysts, and they each have different catalytic activities. FAU zeolite, which is the primary active compound of FCC catalysts, has a relatively large pore size, with a 12-ring of oxygen atoms, and it shows catalytic activity for bimolecular reactions including hydrogen transfer and cracking through the bimolecular intermediate as well as monomolecular cracking and isomerization of hydrocarbons. MFI zeolite is used as an additive to the FCC catalyst for the purpose of increasing light olefin yields and octane value of gasoline fractions [2]. It shows high catalytic activity for the cracking of C7+ olefins into LPG range olefins and isomerization of n-olefins into i-olefins, while bimolecular reaction is not allowed because of its small pore size with a 10-ring of oxygen atoms [3]. Furthermore, the small pore size restricts the entry of large branched hydrocarbons; therefore, the active sites of MFI zeolite are only accessible for linear and monomethyl molecules [4].

Synergetic effects through mixing FAU zeolites and MFI zeolites are reported in some literature [5–10]. Pzikh et al. [5] observed the enhancement in the formation of branched C4 products for the mixture of FAU and MFI zeolites compared to the yield predicted by weighted average of the reaction products on the individual zeolite, which suggests that the reaction products are transferred between FAU and MFI zeolites. The enhancement is ascribed to the light products on MFI zeolites being further isomerized on the FAU zeolites. Den Hollander et al. [9] found that the addition of MFI zeolites to FAU zeolites leads to an increase of LPG range olefins and paraffins, while it decreases the yield of branched products in gasoline ranges in the cracking of hydrotreated distillate. This is because MFI zeolites crack feedstock-range hydrocarbons into LPG range olefins after the pre-cracking of paraffinic feedstock by FAU zeolites. Part of the olefins produced on MFI zeolites are converted to paraffins by hydrogen transfer reaction on FAU zeolites. These observations suggest that the addition of MFI zeolites to FAU zeolites is effective for octane boosting of produced gasoline fractions because it can crack long chain molecules which show low octane value.

However, the cracking of long chain molecules in gasoline range into LPG range olefins is associated with decrease of gasoline yield. To solve this trade-off, Buchannan [11,12] investigated the effect of the addition of MFI zeolites with high Si/Al ratio. It resulted in an acceleration of the rate of
isomerization, which could boost octane value with no gasoline yield loss, rather than cracking of C5-C7 olefins or reducing gasoline yield. Therefore, MFI zeolites with high Si/Al ratios can be adopted as octane boosting additives with small gasoline yield loss.

Recently, the FCC reaction activity of *BEA zeolites have been investigated [13–17]. *BEA zeolites have a large pore size with a 12-ring of oxygen atoms, and they show catalytic activity for the cracking and isomerization of paraffins, while they are not so active for hydrogen transfer reactions [13]. Pusparatu et al. [14] observed the enhancement of the ratio of isomerization to cracking by increasing Si/Al ratios of *BEA zeolites. Furthermore, the ratios in *BEA zeolites was higher than that in MFI zeolites. These findings suggest that *BEA zeolites with high Si/Al ratios are suitable as additives to FAU zeolites, which is expected to boost octane value without sacrificing gasoline yield. Therefore, in this study, we investigated the addition of *BEA zeolites with high Si/Al ratios to FAU zeolites in n-hexadecane cracking as a model reaction of heavy oil cracking and compared the effect of the addition of *BEA zeolites to MFI zeolites. In addition, in order to enhance the synergetic effect of FAU zeolites and additives, composite catalysts that contains both FAU zeolites and additive zeolites in a single particle were prepared and used for catalytic cracking experiments, although most literature deals with synergetic effects of FAU and MFI zeolites in physical mixtures or sequential catalyst beds of separate catalysts.

2. Results and Discussion

2.1. Catalyst Characterization

Figure 1 shows the XRD patterns of the synthesized zeolite catalysts. Diffraction peaks at around 7.5° and 22.5° observed in the *BEA386 sample are characteristic peaks of the BEA zeolite [18]. The diffraction patterns of the MFI zeolite samples shown in Figure 1 also agreed with the pattern of the MFI zeolites reported in the literature [19]. From these results, it was confirmed that the desired zeolite catalysts were obtained in this study.

![Figure 1. XRD patterns of the synthesized zeolite samples.](image-url)
2.2. Catalytic Cracking Test

The RFCC catalyst, the *BEA catalysts, and the composite catalysts (RFCC + *BEA, RFCC + MFI) were tested for catalytic cracking of $n$-hexadecane. Reaction products were classified into gas ($C_1$–$C_4$), gasoline ($C_5$–$216^\circ\text{C}$), light cycle oil (LCO, $>216^\circ\text{C}$) and coke. Most of the components in LCO fractions were unconverted $n$-hexadecane and the yield of other reaction products in LCO fractions was lower than 5%, which suggests that $n$-hexadecane was mainly cracked into gas, gasoline and coke. The yields of gas, gasoline and coke are shown in Figure 2. Compared with the RFCC catalyst, the *BEA catalysts showed lower gasoline yield and higher gas and coke yield. However, the yield of gas, gasoline and coke on the composites of the RFCC catalyst and the *BEA zeolite were close to those on the RFCC catalyst, which means that addition of the *BEA zeolite hardly affects the yield of each fraction. On the other hand, the addition of the MFI zeolite to the RFCC catalyst slightly decreased the gasoline yield and increased the gas yield. This result indicates that the gasoline fraction compounds produced by the cracking of $n$-hexadecane on the RFCC catalyst were transferred to the MFI zeolite and overcracked into the gas fraction. The coke yield on the RFCC catalyst was hardly affected by the addition of the MFI zeolite.

Figure 3 shows the yield of the products in the gasoline fraction obtained from the $n$-hexadecane cracking on different catalysts. On all the catalysts, the paraffins and aromatics increased with the increase in the $n$-hexadecane conversion, while the olefins decreased drastically at high $n$-hexadecane conversion. This is because the hydrogen transfer reaction is activated under the severe reaction condition, which results in the conversion of olefins into paraffins and aromatics by the following reaction.

\[
\text{olefin} + \text{olefin} \rightarrow \text{paraffin} + \text{aromatics}
\]  

(1)

As shown in Figure 3, the addition of the *BEA or MFI zeolites to the RFCC catalyst increased the olefin yields while it decreased the paraffin yields. Among them, the increase in the olefin yields by the addition of *BEA386 was remarkable. These results can be ascribed to the lower activity of the *BEA and MFI zeolites for the hydrogen transfer reaction than those of the RFCC catalyst. Especially, the *BEA386 contains very few acid sites on the outer shell of the particle because it was synthesized by a two-step crystallization method in which the aluminum source was not added at the second crystallization step as shown in the experimental section. Therefore, it can be assumed that the *BEA386 zeolite produces a low level of activity in the hydrogen transfer reaction which results in the high olefin yield. To confirm this assumption, the butene/butane ratio obtained from the $n$-hexadecane cracking, which is an index representing the hydrogen transfer activity [20], were compared in Figure 4. The butene/butane ratios on the composite catalysts were higher than those on the RFCC catalyst, especially at a lower conversion, which indicates the lower hydrogen transfer reaction activity.
Figure 2. Reaction product yields of $n$-hexadecane cracking on the RFCC and the composite catalysts. (a)(b) Gas yield. (c)(d) Gasoline yield. (e)(f) Coke yield. (a)(c)(e) Reaction product on the *BEA catalyst and the composite catalyst with the *BEA zeolite. (b)(d)(f) Reaction product on the composite catalyst with the MFI zeolite.
Figure 3. Yields of the products in the gasoline fractions. (a)(b) Paraffin yield. (c)(d) Olefins yield. (e)(f) Monoaromatics yield. (a)(c)(e) Reaction product on the *BEA catalyst and the composite catalyst with the *BEA zeolite. (b)(d)(f) Reaction product on the composite catalyst with the MFI zeolite.
Figure 4. Butene/butane ratio of the reaction product on the composite catalysts. (a) Reaction product on the *BEA catalyst and the composite catalyst with the *BEA zeolite. (b) Reaction product on the composite catalyst with the MFI zeolite.

Figure 5 shows the branching degree of the paraffins in the gasoline fractions. Compared with the RFCC catalyst, the *BEA catalysts were less active for isomerization of paraffins in gasoline fractions. However, the change of product distribution by the addition of the *BEA zeolites to the RFCC catalyst was different from the product distribution predicted by weighted average of the reaction products on the RFCC catalyst and the *BEA catalysts. Addition of the *BEA zeolite to the RFCC catalysts decreased the single-branched paraffins slightly and increased the multi-branched paraffins, while the n-paraffin yield was not affected. This result suggests that the *BEA zeolites catalyze the isomerization of single-branched paraffins produced on the RFCC catalyst into multi-branched paraffins. The addition of *BEA386, which contains less acid site on the outer shell of the particle, was especially effective for increasing the yield of multi-branched paraffins. On the other hand, the addition of the MFI zeolites to the RFCC catalyst led to different changes of product distribution. The yield of n-paraffins and single-branched paraffins decreased with the MFI zeolite addition, while that of multi-branched paraffins was not affected. This may be because n-olefins and single-branched olefins produced on the FAU zeolites were transferred to the MFI zeolites and overcracked into gas fraction, while multi-branched olefins were not able to diffuse into the MFI zeolite pores because of steric hindrance. Therefore, few of the n-olefins and single-branched olefins were available for conversion to n-paraffins and single-branched paraffins by hydrogen transfer reaction on the FAU zeolites. From the results of Figure 2, 3, and 5, it is concluded that the *BEA zeolites are active for the isomerization reaction while the MFI zeolites are active for the cracking reaction. Both zeolites are less active for the hydrogen transfer reaction than the FAU zeolite.

Figure 6 shows the research octane number (RON) of the gasoline fraction obtained with the RFCC and the composite catalysts. The composite catalysts showed a higher RON value than the RFCC catalysts. However, factors that contribute to the octane boosting are different between the additives. Enhancement of RON value by the addition of *BEA zeolite is attributed to preventing the loss of olefins by a strong hydrogen transfer reaction on FAU zeolites and accelerating the isomerization of single-branched molecules into multi-branched molecules. This result suggests the possibility for increasing the octane value of the gasoline produced from the catalytic cracking of heavy oils without sacrificing the gasoline fraction yields, even under the reaction conditions with high hydrogen transfer.
Catalysts 2015, 5, 710

activity. In contrast, RON increase by the addition of MFI zeolites can be explained by a decrease of \( n \)-paraffins and single-branched paraffins which have low octane value as shown in Figure 5. In this mechanism of octane boosting, the simultaneous loss of gasoline yield is unavoidable.

![Figure 5](image)

**Figure 5.** Yields of the paraffin products in the gasoline fraction. (a)(b) Linear paraffin yield. (c)(d) Single-branched paraffin yield. (e)(f) Multi-branched paraffin yield. (a)(c)(e) Reaction product on the *BEA catalyst and the composite catalyst with the *BEA zeolite. (b)(d)(f) Reaction product on the composite catalyst with the MFI zeolite.
2.3. Reaction Mechanism on the Composite Catalyst

In this section, we discuss the reaction scheme for the catalytic cracking of \( n \)-hexadecane on the RFCC and the composite catalysts. As shown above, the addition of the *BEA or MFI zeolites to the RFCC catalyst caused the change of the product distribution of the \( n \)-hexadecane cracking such as (i) an increase in the yield of olefins in the gasoline fraction on both additives, and (ii) an acceleration of isomerization which resulted in the increase in the yield of multi-branched paraffins on the *BEA zeolites, while the cracking of linear and single-branched olefins were accelerated on the MFI zeolites. Considering these results, a schematic reaction mechanism on the composite catalysts can be proposed as shown in Figure 7.

According to the carbenium ion mechanism, which is a generally accepted theory of the acid-catalyzed cracking [21], the reaction route of the \( n \)-hexadecane cracking on the FAU zeolites is as follows. The feedstock paraffin molecules diffuse into the zeolite pores (R1) and react with the carbenium ions adsorbed on the acid site (R2). Hydride ions are transferred from the paraffins to the carbenium ions and produce small paraffins and large, new carbenium ions. Then, the \( \beta \)-scission of the large carbenium ions proceeds and form olefins and small carbenium ions (R3). These small carbenium ions are consumed in the hydride-transfer reactions of the next feedstock molecules (R2), and therefore, the cracking of the feedstock continues. The produced olefins adsorb again on the acid sites and forms carbenium ions (R4), which are further cracked into gas fractions (R5) or isomerized into branched olefins (R6, R10). In addition, if the two carbenium ions adsorb on the adjacent acid site, a hydrogen transfer reaction proceeds and the active olefins are converted into the stable paraffins and aromatics, which prohibits the overcracking of the gasoline fractions (R7, R11, R14). Because the FAU zeolites have high hydrogen transfer activity, the gasoline fraction on the RFCC catalyst includes a large amount of paraffins as shown in Figure 3.
In the case of the composite catalysts, however, the cracking of the feedstock molecule proceeds on the two parts of the catalyst that have different catalytic activities. As mentioned above, the *BEA zeolites have lower hydrogen transfer activity than the FAU catalysts in the RFCC catalyst. Therefore, it is more difficult to initiate the cracking of feedstock paraffins on *BEA zeolites than on FAU zeolites, even if \( n \)-hexadecane can diffuse into the pores, because the bimolecular cracking hardly proceeds on the *BEA zeolites. The reason for the higher yield of olefins on the composite catalysts shown in Figure 3 is assumed to be that the gasoline fraction olefins produced from the \( \beta \)-scission on the acid site of the FAU zeolites diffuse into the *BEA zeolites and become stable by being isolated from the strong catalytic activity for cracking and the hydrogen transfer reaction on the FAU zeolites (R15a, R18a, R21a). This is confirmed by the remarkable increase in the yield of olefins by the addition of *BEA386 zeolite, even though it contains very few acid sites on the outer shells of the particle. In addition, the isomerization of the olefins transferred from the FAU zeolites to the *BEA zeolites proceeds on the *BEA zeolites with high Si/Al ratios and the multi-branched olefins are produced (R17a, R20a) [14]. These multi-branched olefins are transferred into the FAU zeolites again (R21a) and converted to the multi-branched paraffins via hydrogen transfer reaction (R14). This scheme can...
explain the increase in the yield of the multi-branched paraffins by the addition of the *BEA zeolites to the RFCC catalyst. The effect could be especially enhanced for the *BEA386. Here, the ramification of carbenium ions is thermodynamically favorable, while the cracking of ramified carbenium ions also proceeds more rapidly than that of linear ions [22]. Therefore, increasing the yield of multi-branched molecule requires reaction control, which only enhances isomerization reactions and suppress cracking. From the results shown in Figure 5, the *BEA386 with less acidity is suitable for the reaction control because the isomerization requires far less catalyst acidity than cracking.

On the other hand, the reaction on the additives is different in the case of the addition of MFI zeolites. Firstly, the MFI zeolites are not active for hydrogen transfer reaction, which is in common with the *BEA zeolites. Therefore, olefins become stable by the addition of the MFI zeolites to the RFCC catalyst as shown in Figure 3. The difference between *BEA and MFI zeolites is their pore size and selectivity of the reactions. Because of the small pore size of MFI zeolites, only linear and single-branched molecules can diffuse into the active site of the additives (R15b, R18b) [4]. In the pore of MFI zeolites, cracking of the olefins into gas fractions is more active than isomerization because the formation of multi-branched molecules is prohibited by steric hindrance. Therefore, the n-paraffins and single-branched paraffins in gasoline fractions are decreased by the MFI zeolite additions as shown in Figure 5. Consequently, as the additive to the RFCC catalyst, *BEA zeolites are active in the isomerization of the gasoline range molecules, while the MFI zeolites are active in the cracking of linear and single-branched molecules in gasoline fractions.

3. Experimental Section

3.1. Zeolite Synthesis

In this study, both synthesized and commercially produced zeolites were used as an additive to the RFCC catalyst. With regard to the *BEA zeolite synthesis, we referred to the method described in the U.S. patent [23].

At first, we tried to synthesize *BEA zeolites that do not contain aluminum because we needed to investigate the reaction on *BEA zeolites with high Si/Al ratios. However, the crystallization of *BEA zeolites did not proceed from the feedstock mixtures without an aluminum source and the obtained powder was in an amorphous state. Therefore, *BEA zeolites with high Si/Al ratios were synthesized by two-step crystallization method as follows. In the first step, the mixture of aluminum nitrate nonahydrate, sodium silicate gel, sodium hydrate, tetraethylammonium hydroxide, and distilled water was charged into Teflon-lined stainless steel autoclaves and crystallized by hydrothermal treatment at 150 °C for several days. The product of the hydrothermal synthesis was washed, filtered, dried and calcined at 550 °C in air atmosphere. In the second step, in order to prepare the *BEA zeolites with high Si/Al ratios, the obtained zeolite powder was again mixed with the starting materials without an aluminum source and hydrothermally treated at 140 °C for two days. The obtained zeolite powder was washed, filtered, dried, and calcined. By this preparation method, the obtained *BEA zeolites are expected to have a core-shell-like structure, i.e., the inside core of the particles contain Al species, while the outer shell hardly contains them. The overall Si/Al ratios of the obtained *BEA zeolites were 386, which was calculated with the weight ratio of the feedstock loaded in the autoclave. However, the
outer shell of the zeolite, which is the main part where the catalytic reaction proceeds, is expected to have catalytic properties with higher Si/Al ratios than the ratios of the zeolites overall. This zeolite powder was used as an additive to the RFCC catalyst as well as the commercially produced *BEA zeolites with Si/Al ratios of 500. The synthesized and commercially produced *BEA zeolites are denoted as *BEA386 and *BEA500, respectively.

MFI zeolites were synthesized as follows. The mixture of aluminum nitrate nonahydrate, colloidal silica, tetrapropylammonium bromide, sodium hydrate, sodium chloride and distilled water was charged into Teflon-lined stainless steel autoclaves and hydrothermally treated at 180 °C for 3 days. The product was washed, filtered, dried and calcined at 550 °C in air atmosphere. The MFI zeolites with Si/Al ratios of 1000 and 2450 were synthesized and used as well as commercially produced MFI zeolites with Si/Al ratios of 50, 280, and 1500. All of these MFI zeolites are denoted as MFI\_X, where X represents the Si/Al ratio.

The synthesized zeolite samples were characterized by the X-ray diffraction (XRD) using an RINT 2550 (Rigaku Co., Japan) with Cu K\_\text{\(\alpha\)} radiation.

3.2. Catalyst Preparation

The *BEA or MFI zeolites were mixed with distilled water, alumina binder, and the commercial RFCC catalyst containing FAU zeolites of approximately 30 wt.%. The mixture was kneaded and calcined at 600 °C. Table 1 shows the composition of the composite catalyst. The obtained catalysts were ion-exchanged with an aqueous solution of NH\text{\textsubscript{4}}NO\text{\textsubscript{3}} and calcined in air at 550 °C to be transformed into proton form. The catalysts were crushed and sieved to a particle size range of 45–150 µm. Before the catalytic activity test, the catalysts were hydrothermally deactivated with a fluidized bed reactor in 100% steam atmosphere at 800 °C for 3-12 h in order to simulate the equilibrium catalyst in the actual FCC process. In addition, for the purpose of measuring the catalytic cracking activity of the *BEA zeolites alone, the *BEA catalysts, which do not contain FAU zeolites, were prepared from the mixture of the *BEA zeolites, distilled water, alumina binder, and Kaolin. The following procedure of the *BEA catalyst was same as the composite of the RFCC catalyst and the *BEA zeolites.

<table>
<thead>
<tr>
<th>*BEA or MFI zeolite</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>RFCC catalyst</td>
<td>75</td>
</tr>
<tr>
<td>Colloidal alumina</td>
<td>10</td>
</tr>
</tbody>
</table>

3.3. Catalytic Activity Test

In this study, n-hexadecane was used as a model compound of heavy crude oil. Catalytic activity tests were conducted in a fixed bed microactivity test (MAT) reactor described by ASTM (No. D3907-92) [24]. Reaction procedure followed the ASTM (No. D5154-10) [25]. Figure 8 shows the experimental set-up. The steam-equilibrated catalyst was placed in a reactor maintained at 495 °C by a three-zone electric furnace. The feedstock was fed by a microfeeder and heated electrically in a preheating line. The weight ratio of the catalyst to the oil (cat/oil) was varied between 0.75–6.0. During the feed injection, N\text{\textsubscript{2}} was used as an added gas (15 mL min\textsuperscript{-1}) and a purge gas (5 mL min\textsuperscript{-1}). After the reaction, stripping
of the catalyst was carried out with the purge gas for 15 min. During the reaction and stripping steps, the liquid products were collected in a receiver and a trap, which were kept at 0 °C with an ice water mixture and −15 °C with an ethylene glycol-water mixture, respectively. Meanwhile the gaseous products were collected in a gas burette by water displacement.

![Figure 8. Schematic representation of the microactivity test reactor.](image)

The reaction products were analyzed with gas chromatographs. H₂ and N₂ in the gaseous products were analyzed with a gas chromatograph (GC-390B, GL Science Inc., Japan) equipped with a packed column (MS13X) and a thermal conductivity detector (TCD) using Ar as a carrier gas. The gaseous and liquid hydrocarbons were analyzed with a gas chromatograph (GC-2014, Shimadzu Co., Japan) equipped with a capillary column (60 m × 0.25 μm, BP1) and a flame ionization detector (FID) using He as a carrier gas. The coke contents formed over the catalyst during the reaction were analyzed with an NC analyzer (SUMIGRAPH NC-1000, Sumika Chemical Analysis Service, Ltd., Japan).

4. Conclusions

Multifunctional catalysts were developed by adding *BEA or MFI zeolites to the RFCC catalyst and then tested in the catalytic cracking of n-hexadecane. The addition of *BEA zeolites with high Si/Al ratios did not affect the gasoline yield, while the addition of MFI zeolites overcracked the gasoline fractions and increased gas yield. The composite of the RFCC catalyst and the high Si/Al ratio *BEA zeolites showed higher yields of olefins and multi-branched paraffins compared to the RFCC catalyst, which resulted in the improvement of the octane value without sacrificing gasoline yield. In general, multi-branched molecules are more easily cracked than linear molecules, which makes it difficult to increase the yield of multi-branched molecules. Our results suggest the possibility for the selective acceleration of isomerization reaction in the catalytic cracking of heavy oil by the addition of less acidic *BEA zeolites to the RFCC catalyst.
Acknowledgments

This work was supported by the Japan Petroleum Energy Center (JPEC) as a technological development project supported financially by the Ministry of Economy, Trade and Industry, which are greatly appreciated.

Author Contributions

I. Shimada analyzed the experimental data and wrote the paper. R. Imai and Y. Hayasaki conducted the catalytic activity tests and the reaction products analysis of the composite catalysts of *BEA and MFI zeolites, respectively. H. Fukunaga and N. Takahashi advised about the experiments and data analysis through the discussions, and T. Takatsuka supervised this study.

Conflicts of Interest

The authors declare no conflict of interest.

References


© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).