



# Catalytic cracking of polycyclic aromatic hydrocarbons with hydrogen transfer reaction



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## ABSTRACT

With the aim of enhancing oil refining processes based on fluid catalytic cracking (FCC), the catalytic cracking of polycyclic aromatic hydrocarbons (PAHs) was investigated using an FCC catalyst consisting of a rare earth ion exchanged USY zeolite. In these trials, model PAHs were dissolved in *n*-hexadecane and were fed into a fixed bed microactivity test reactor operating at 516 °C. Reaction product analysis indicated very little cracking of the 2-ring PAH over the FCC catalyst, while in contrast the 3-ring PAH was highly reactive, and was rapidly converted into monocyclic aromatic hydrocarbons, 2-ring PAHs and coke. Tests using FCC catalysts with different rare earth loadings revealed that the loading amount has little effect on the conversion of the 3-ring PAH. In addition, catalysts containing USY zeolites with comparable unit cell sizes, and thus having comparable hydrogen transfer activities, exhibited similar catalytic activities for 3-ring PAH conversion, even though they contained different amounts of the rare earth metal oxide. This result suggests that the hydrogen transfer reaction plays an important role in 3-ring PAH conversion and that the main effect of rare earth loading is to maintain the hydrogen transfer activity of the catalyst by stabilizing the USY zeolite against steam deactivation. In summary, this study successfully demonstrated a potential FCC process for converting PAHs into useful light fractions without the necessity of employing a pressurized hydrogen atmosphere.

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## 1. Introduction

Increasing refining capacity and expanding the range of heavy crude oils that may be processed are both important components of the efficient use of oil resources. To achieve these objectives, it is necessary to decompose the polycyclic aromatic hydrocarbons (PAHs) contained in heavy crude oils into valuable light fractions, such as gasoline. In modern petroleum refineries, the cracking of high molecular weight components is performed using the fluid catalytic cracking (FCC) process. Unfortunately, the FCC process has been considered not to be able to directly refine PAHs because of the difficulty associated with activating aromatic rings in the catalytic cracking reaction [1,2]. Therefore, to obtain the most efficient utilization of heavy crude oils, it has been considered necessary to hydrogenate PAHs so as to convert them into naphthenes through a hydrodesulfurization pretreatment before they are supplied to the FCC process. While the hydrogenation of PAHs through hydrodesulfurization takes place at high hydrogen partial pressures, this same reaction has not been observed in the FCC process,

because in the FCC process the equilibrium between the hydrogenation of aromatic hydrocarbons and the dehydrogenation of naphthenes is highly biased toward the dehydrogenation reaction at high temperatures and low hydrogen partial pressures. On the other hand, in the FCC reaction, there is a transfer of hydrogen atoms between donors and acceptors through the hydrogen transfer reaction. The hydrogen transfer reaction is an important aspect determining the quality of the resulting gasoline product because it is responsible for suppressing overcracking of the gasoline fraction and stabilizing the desired compounds through the saturation of olefins and the generation of aromatics by transferring hydrogen atoms from naphthenes to olefins. Nevertheless, the hydrogen transfer reaction is still considered undesirable and has been suppressed by recent catalyst designs because the conversion of olefins into paraffins results in the production of gasoline with a lower octane number [3,4]. However, given that the activation of the hydrogen transfer reaction contributes to the decomposition of PAHs in the FCC process, drastic changes would be allowed to the design of FCC catalysts, which makes it possible to treat heavy crude oils via a simple process that does not require pretreatment.

To date, investigations of the hydrogen transfer reaction over USY zeolites, which are the main active components of FCC

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catalysts, have been widely reported in the literature. Pine et al. [5] have suggested that the hydrogen transfer reaction is a bimolecular reaction in which hydrogen atoms are transferred between molecules adsorbed on adjacent acid sites of the zeolite catalyst. Therefore, the activity of the catalyst greatly depends on the density of aluminum sites because the number of Brønsted acid sites, representing the active sites for hydrogen transfer, is related to the number of framework aluminum atoms [6]. In contrast, Corma et al. [3,7] have concluded that observed changes in the reaction product distribution over catalysts with different Si/Al ratios is the result of the varying hydrophobicities of the catalyst surfaces. In fact, the adsorption of olefins (more highly polar products) relative to paraffins (less polar) decreases on the hydrophobic surfaces associated with high Si/Al ratios. Therefore, the hydrogen transfer reaction, which necessarily involves olefins, proceeds less favorably compared to the cracking of paraffins when employing catalysts with high Si/Al ratios. Both these literature reports suggest that hydrogen transfer activity is significantly affected by the density of the aluminum sites in the unit cell of the USY zeolite. Pine et al. [5] also proposed that the hydrogen transfer activity can be correlated with a single parameter, the unit cell size (UCS), because the UCS provides a measure of the total number of tetrahedral aluminum sites per unit cell. The relationship between the UCS and the hydrogen transfer activity has been reported in several literature publications [4,8,9].

Although accelerating the hydrogen transfer activity requires a high density of aluminum sites, the FCC catalyst is exposed to high temperature steam during the regeneration cycle of the FCC process, and this tends to dealuminate the zeolite framework [10,11]. Therefore, even if the fresh FCC catalyst exhibits high hydrogen transfer activity, the activity of the equilibrated catalyst is lessened due to the dealumination accompanying this severe regeneration treatment [8]. To prevent the aluminum loss and enhance the structural stability of USY zeolite, the introduction of rare earth (RE) metal ions has been found to be effective [12]; RE loading stabilizes the UCS of the USY zeolite during steam treatment [4,8,13] and maintains hydrogen transfer activity during hydrocarbon cracking [14]. Based on the above, the present work examined the catalytic cracking of PAHs on an FCC catalyst with RE loading and investigated the effects of the hydrogen transfer reaction on the conversion of PAHs during the FCC reaction.

## 2. Materials and methods

Commercial FCC catalysts consisting of USY zeolite with high (several percent) and low (a very small amount) RE metal oxide loading were supplied by Grace Davison. Prior to catalytic activity tests, the catalysts were hydrothermally deactivated in a fluidized bed reactor under a 100% steam atmosphere at 800 °C for 3–12 h (steam deactivation) until the UCS of each catalyst was stable. The steam-equilibrated catalysts were characterized by X-ray diffraction (XRD) using a RINT 2550 instrument (Rigaku Co., Japan) with Cu K $\alpha$  radiation. The UCS value of each catalyst was calculated from the diffraction peaks of the (533) and (642) planes.

The compounds 1-methylnaphthalene (1-MN), 9-methylanthracene (9-MA) and *n*-hexadecane (*n*-HD) were used as models of the 2-ring PAH, 3-ring PAH and paraffin components in heavy crude oils, respectively. Test samples were made by dissolving each model PAH in *n*-HD at a molar ratio of 20:80. Catalytic activity tests were conducted in a fixed bed microactivity test (MAT) reactor that has been described in a previous publication [15]. In each trial, 4 g of the steam-equilibrated FCC catalyst was placed in the reactor, maintained at 516 °C using a three-zone electric furnace, following which a solution of one of the model PAHs in *n*-HD was fed into the reactor by a microfeeder while being heated electrically in a

preheating line. The feed injection time was 75 s and the weight hourly space velocity (WHSV) was varied between 12 and 24 h<sup>-1</sup>, corresponding to the weight ratio of the catalyst to the oil (cat/oil) ranging from 2 to 4. N<sub>2</sub> gas was added during the feed injection at 20 ml min<sup>-1</sup>. Following each reaction, the catalyst was stripped with N<sub>2</sub> purge gas (5 ml min<sup>-1</sup>) for 15 min. During the reaction and stripping steps, the liquid products were collected in both a receiving vessel and a trap, maintained at 0 °C with an ice-water mixture and at -15 °C with an ethylene glycol-water mixture, respectively. Simultaneously, the gaseous products were collected in a gas burette by water displacement.

The reaction products were analyzed by gas chromatograph (GC). H<sub>2</sub> and N<sub>2</sub> in the gaseous products were determined using a GC (GC-390B, GL Science Inc., Japan) equipped with a packed column (MS13X) and a thermal conductivity detector (TCD), using Ar as the carrier gas. The gaseous and liquid hydrocarbons were also assessed with a GC (GC-2014, Shimadzu Co., Japan), but using a capillary column (BP1) and a flame ionization detector (FID) with He as the carrier gas. In addition, the liquid hydrocarbons were analyzed with another GC (GC-7890, Agilent Technologies Inc., USA) equipped with a mass spectrometer (JMS-Q1000GC, JEOL Ltd., Japan). 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).

Reaction products were classified by their number of carbons or boiling points into the following groups, which are typical of the FCC process: dry gas (C<sub>1</sub>–C<sub>2</sub>), liquefied petroleum gas (LPG, C<sub>3</sub>–C<sub>4</sub>), gasoline (C<sub>5</sub>–216 °C), light cycle oil (LCO, 216 °C–) and coke. In this work, 216 °C conversion was defined as the weight percentage of the sum of the dry gas, LPG, gasoline and coke in the products relative to the LCO fraction in the feed, and was adopted as an index of reaction severity. It should be noted that the feedstock we used in this study (1-MN, 9-MA and *n*-HD) would be classified as belonging to the LCO fraction.

In this paper, we focus on the conversion of PAHs during the catalytic cracking reaction, and therefore we define the PAH conversion ratio by the following equation.

$$R_n = \frac{M_{n,0} - M_n}{M_n} \times 100 \quad (1)$$

Here, *n* represents the number of aromatic rings in the PAH model compound in the feedstock (*n* = 2 for the 1-MN/*n*-HD mixture; *n* = 3 for the 9-MA/*n*-HD mixture), *R<sub>n</sub>* represents the conversion ratio of the *n*-ring PAH, and *M<sub>n,0</sub>* and *M<sub>n</sub>* represent the sum of the amount of the *n*-ring PAHs on a molar basis in the feed and product, respectively. It should be noted that the value of *R<sub>n</sub>* was calculated on a molar basis because a molar-based unit represents the number of aromatic rings and is not affected by alkylation of the PAHs during the reaction.

## 3. Results and discussion

### 3.1. Catalytic cracking of polyaromatic hydrocarbons

The catalytic cracking of PAHs was investigated using the FCC catalyst with a high RE loading after the catalyst was steam deactivated at 800 °C for 12 h. The unit cell size of the USY zeolite in the catalyst was reduced to 24.29 Å by the deactivation. Table 1 shows the conversion of each feedstock over this catalyst, and it is evident that the 216 °C conversion, as well as the *n*-HD, 1-MN and 9-MA conversions, increased monotonically with increases in the cat/oil ratio. This result demonstrated that the 216 °C conversion can represent the severity of the reaction conditions, and so we subsequently adopted the 216 °C conversion as an index of the reaction severity. The *n*-HD conversions during the cracking of

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