Catalytic cracking of soybean oil by hierarchical zeolite containing mesoporous silica-aluminas using a Curie point pyrolyzer

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ABSTRACT

Catalytic cracking of soybean oil using hierarchical zeolite-containing mesoporous silica-aluminas was successfully estimated using a Curie point pyrolyzer. Most of the prepared catalysts exhibited higher catalytic activity and selectivity for gasoline than did a simple zeolite. The catalysts prepared using a larger amount of malic acid developed mesoporous structures and showed higher olefin/paraffin ratios and research octane numbers (RONs) than the simple zeolite and a catalyst with a microporous structure. When β zeolite-containing catalysts were used, the ratio of multi/single branched products in the gasoline fraction reached more than 0.40, which was considerably larger than that obtained using a simple zeolite. When the yields of gasoline, single-branched products and multi-branched products were plotted against the conversion of soybean oil, approximately linear relationships were observed for every plot. When the yields of gasoline and single-branched products were compared at the same conversion, the yields from the HY zeolite-containing catalysts were higher than those from the β zeolite-containing catalysts. These results were consistent with those for the catalytic cracking of VGO previously reported. However, the yields of multi-branched products from β zeolite-containing catalysts were higher than those from HY zeolite-containing catalysts. This result was different for VGO cracking, where the yield of multi-branched products from HY zeolite was higher. Furthermore, the RON of gasoline and the yield of aromatic compounds were higher than those for the catalytic cracking of VGO.

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1. Introduction

Considerable attention has been focused on the utilization of fatty acid methyl ester (FAME), a carbon neutral biodiesel that is produced by transesterification of fat with methanol; however, it is noted that there are problems in the quality of FAME [1]. FAME still has a relatively high boiling point as a gas oil fraction, although it is lighter than the original fat. Furthermore, if any glycerol byproducts, unreacted methanol or alkali catalysts remain in the FAME, they may have negative effects on the combustion of the fuel. A surplus of glycerol, which is obtained at 10% yield, takes up a lot of space. Recently, many studies have been devoted to not only the direct hydrocracking of fats to obtain diesel fuels with high cetane numbers [2–4] but also the catalytic cracking of fats to obtain gasoline with a high octane number and an appropriate boiling range [5–11]. Not glycerol but propane and propene, which are easily

used as fuel and raw material for petrochemicals, can be obtained in hydrotreating and catalytic cracking. Because the boiling range of a fat is similar to that of atmospheric residue (AR), it is expected that fat can be used in a petroleum refinery by mixing with AR or vacuum gas oil (VGO). Specifically, catalytic cracking is a promising method for obtaining gasoline with high octane numbers because fat includes a large number of unsaturated bonds in its alkyl chains, which have good potential to give aromatics and olefins with high octane numbers.

In recent years, catalytic cracking has remained one of the most important research areas, where not only micropores of zeolites but also mesopores of matrices are newly prepared, and their properties for the catalytic cracking of real feeds or model compounds are discussed. Therefore, the development and modification of zeolites has been a major part of the development of catalytic cracking catalysts. To transfer larger molecules, such as VGO or AR, and to increase the speed of diffusion in a catalyst, it was noticed that the introduction of mesopores into catalysts would be needed. The direct introduction of mesopores into zeolite scaffolds is promising, and a number of attempts have been

made to introduce mesopores into zeolites. For examples, desilication [12–14], dealumination [15,16] and the use of templates, such as modified carbon [17], polymers or organosilane compounds [18–21], have been reported; however, there may be limitations on the modification of zeolite crystals because these experiments decomposed the crystal structures of common zeolites. Furthermore, the relative amounts of mesopores are usually smaller than those of micropores, and mesopores are surrounded by micropores. In such situations, diffusion limitation is still a serious problem because the products would encounter micropores at the final stage of the reaction. As an alternative, the most effective method includes the combination of various matrices with zeolite. Mesoporous matrices play a very important role in the rapid diffusion of substances. Recently, many studies have been devoted to the preparation of meso-/microporous composite materials [22–27]. The formation of hierarchical composite catalysts with both zeolite and mesoporous materials may give rise to the possibility of increasing branched products with the higher octane numbers because the large space in the mesoporous material around an active acid site in zeolite promotes the generation of more bulky branched hydrocarbons. However, it is not completely clear what size of matrix pore or what type of acid sites in the matrix give optimum catalysts with high yields of desirable products, although the effects of the amounts and types of zeolite on catalytic activity and product selectivity in catalytic cracking have been discussed extensively.

We have already reported that mixed catalysts of amorphous mesoporous silica-aluminas and microporous zeolites had higher conversion and product selectivity than simple zeolites or a physical mixture of silica-alumina and zeolite [28–32]. These catalyst systems promoted the formation of branched hydrocarbons, which significantly affect the octane number of gasoline. Hierarchical β and Y zeolite-containing mesoporous silica-aluminas could also be prepared using malic acid (MA) [30]. In these studies, a model compound, n-dodecane, was used as a feed material [28–30]. Furthermore, a novel method to determine the catalytic cracking of VGO using a Curie point pyrolyzer (CPP) was developed as a very simple method for a catalyst evaluation [31,32].

In this study, the catalytic cracking of soybean oil (SBO) using CPP was investigated to estimate the reactivity of hierarchical β and Y zeolite-containing mesoporous silica-aluminas for the catalytic cracking of fat. A simple method to evaluate this reaction is proposed, the specific reactivities of the catalysts are reported, and specifically, the formation of branched products, which has not been described by other researchers, is discussed in detail.

2. Experimental

2.1. Materials

The reagents for the preparation of the gel were tetraethyl orthosilicate (TEOS, Nacalai Tesque Co. Ltd., Kyoto, Japan), aluminum tri-*sec*-butoxide (ASB, Tokyo Kasei Kogyo Co. Ltd., Tokyo Japan), ion-exchanged water (prepared using Auto still AW 200, Yamato Scientific Co. Ltd., Tokyo, Japan), ethanol, 2-butanol (Nacalai Tesque Co. Ltd.) and malic acid (MA, $HOOCCH_2CH(OH)COOH$, Nacalai Tesque Co. Ltd.). Soybean oil (H: 10.95%; C: 76.64%; N: 0.30%; single component: linoleic acid 55%, oleic acid 22%, palmitic acid 11%, stearic acid 4%, linolenic acid 8%) was an extra pure grade of Wako, Tokyo, Japan and was used without further purification. The zeolites used were β zeolite and HY zeolite (β zeolite: SiO_2/Al_2O_3 (mol/mol) 37, Na_2O 0.1 wt%, crystal size 0.05 μm, mean particle size (MPS) 5 μm, cation type H⁺, HSZ-940HOA, Tosoh Corp, Tokyo Japan; HY zeolite: JRC-HY5.5, crystal size 0.2 μm, MPS 6 μm, a reference catalyst in Catalysis Society of

Japan (CSJ), prepared by Tosoh Corp.). For comparison, data for the catalytic cracking of hydrotreated VGO (S 100 ppm) were described [31,32]. The properties of the original VGO supplied from Nippon Ketjen Co. Ltd., Tokyo Japan are as follows: V, Ni 0 ppm; S 2.85%; C 85.48%; H 11.60%; Asphaltene 0.18%; IBP 281 – FBP 570 °C; Dens. AP15 °C 0.9554 g/ml; Vis. 50 °C 47.36 cSt).

2.2. Catalyst preparation

β and Y zeolite-containing silicas and silica-aluminas were prepared using the sol–gel method and malic acid in one pot. The preparation method of hierarchical composites of zeolite-containing silica and silica-alumina was described in detail elsewhere [30–32]. A typical method follows: TEOS was added to a suspension of zeolite in ethanol and the mixture was stirred for 1 h at 25 °C. Next, an aqueous solution of malic acid was added dropwise, and the mixture was stirred for 30 min. Then, a solution of ASB in 2-butanol was added dropwise, and the mixture was stirred for another 30 min. The gelation was performed at 60 °C. The gelation was considered completed when the stirrer tip stopped. The resulting gel was held at 60 °C for 24 h. Finally, the sample was calcined at 600 °C (heating rate 2.5 °C/min) for 3 h in a stream of dried air (600 mL/min). The molar ratio of TEOS:MA:ASB was 1:0.22–1.22:0–0.39. The molar ratio of each catalyst is given in Supplementary Table 1. The catalyst prepared contained 25 wt% of zeolite and 75 wt% of silica-alumina. The alumina content in the silica-alumina component was 0, 1, 5 or 25 wt%. The abbreviation of malic acid (MA), the mole% of MA to TEOS, wt% of alumina in silica-alumina and a type of zeolite appear in naming of the samples. Each catalyst was obtained at greater than 95% yield.

2.3. Characterization of catalysts

The characterization methods were described in detail elsewhere [30–32]. XRD patterns of the samples were obtained using a Rigaku Ultima IV diffractometer. Peaks from β zeolite and Y zeolite crystals and a broad peak of amorphous silica or silica-alumina were observed in each XRD pattern of synthesized zeolite-containing silica and silica-alumina (Supplementary Fig. 1), indicating that crystals of both β and Y zeolites were maintained and dispersed in amorphous silica or silica-alumina, constructing hierarchical structures with microporous zeolite in the centers and mesoporous silica or silica-alumina in the outer shells of the catalysts.

The N_2 adsorption and desorption measurement of a calcined sample was performed using a BELSORP mini II (BEL Japan Inc., Osaka, Japan). The total surface area, pore volume and pore distribution were calculated using the Brunauer–Emmett–Teller (BET) method. To estimate the mesopores, the Barrett–Joyner–Halenda (BJH) method was used. When a large amount of MA with MA/TEOS = 1.22 was used in preparation and the Al_2O_3 content was lower, the catalysts consisted of mainly mesopores, and each catalyst showed clear peaks in BJH pore size distribution plot (Supplementary Fig. 2). When the catalysts barely have any mesopores, the maximum pore sizes calculated using the BJH method were 3.3 nm. In the BJH pore size distribution, Supplementary Fig. 2A, MA122-25-β or simple β zeolite shows no peak but a maximum at 3.3 nm, which was much smaller than those of the other catalysts, MA122-0-β, MA122-1-β and MA122-5-β, indicating that MA122-25-β and simple β zeolite hardly have mesopores. Detailed data appear in Table 1 for the catalysts with β zeolite and Table 2 with Y zeolite.

The amount of NH_3 adsorbed was measured using the pulse method and GC-TCD to determine the amount of acid sites. The amount of NH_3 desorbed was measured by heating the catalyst with