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Catalytic cracking of soybean oil by ZSM-5 zeolite-containing silica-aluminas with three layered micro-meso-meso-structure

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ABSTRACT

In order to convert a large molecule of soybean oil, ZSM-5 zeolite-containing silica-aluminas with three layered micro-meso-meso-structure were developed. In this method, zeolite-containing two layered silica-aluminas initially prepared were combined with silicas having very large mesopores prepared by the gel skeletal reinforcement. The three-layered structure was confirmed by pore size distribution derived from N_2 adsorption and desorption measurements. The catalytic cracking of soybean oil using the three-layered catalysts was evaluated by the Curie point pyrolyzer method. When the reaction was performed at 500 °C, activities of catalysts having hierarchical structures were improved. It is thought that the diffusion of soybean oil molecule was promoted in the presence of large mesopores of the catalysts having hierarchical structure. ZSM-5 zeolite-containing catalysts showed very high research octane number (RON), compared with β zeolite and Y zeolite containing catalysts, indicating that ZSM zeolite-containing catalysts provided gasoline fractions of good quality. Gasoline yields increased with increasing conversion and was plotted on the same straight line when the same type of zeolite was used, indicating that the product selectivity would depend on the type of zeolite and that the activity would strongly depend on the existence of the matrix.

1. Introduction

Although fatty acid methyl ester (FAME) can be produced by transesterification of vegetable oil with methanol, a lot of inconsumable by-product glycerol is formed. Further, FAME, which contains unreacted fatty acid, causes deterioration and corrosion of automobile parts [1]. An alternative ultimate utilization technique of vegetable oil is catalytic cracking to produce bio-gasoline. As a large amount of the unsaturated double bonds are included in vegetable oil, bio-gasoline is considered to have a high octane number. In general, the vegetable oil has a very large molecule which consists of glyceride with three carboxylates of long alkyl chains and its molecular weight is similar to that of atmospheric residue. Therefore, in order to convert the large molecule of vegetable oil, both microporous zeolite and mesoporous matrix are needed simultaneously because micropores would inhibit the diffusion of large molecules. Composite catalysts with zeolites and amorphous silica-alumina are usually used in current catalytic cracking. The presence of such silica-alumina matrices should affect the activity and selectivity of the composite catalysts [2–7]. However, there are very few academic works concerning catalytic properties of the matrices compared to those of zeolites.

Many preparation methods of aluminosilicate or silica-alumina, which can be matrices with mesopores in catalytic cracking, have recently been reported [8–19]. We also developed the preparation technique without use of supercritical fluid, the gel skeletal reinforcement (GSR) method which includes the gel aging in gel-reinforcing agents leading to the maintenance of the original gel framework and the inhibition of the significant shrinkage of pores. When –OH groups at the surface were replaced with trialkoxysilyl or trialkylsilyl groups in the GSR method, further condensation was inhibited and the gel structure was reinforced [2–4]. Using this method, new porous materials with 5 cc/g of pore volume and 40 nm of average pore diameter were prepared [20].

Recently it was shown that two-layered catalysts of both microporous zeolites and mesoporous silica-alumina matrix had very high catalytic activity and product selectivity [4]. Further, when the Y zeolite-containing two-layered catalysts were combined with large pore size of silica prepared by the GSR method to form the three-layered structure, it was found that the activities and selectivities were increased or maintained even if the content of zeolite was decreased to half in catalytic cracking of soybean oil at 500 °C [21]. In this study, in order to confirm this fact, ZSM-5 zeolite-containing three-layered catalysts were prepared and the catalytic cracking of soybean oil was evaluated by Curie point pyrolyzer (CPP) and was compared with those

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using β and Y zeolites. It was demonstrated that CPP provided very easy and convenient method to evaluate the catalytic cracking [4,22,23].

2. Experimental

2.1. Preparation of zeolite-containing three-layered catalysts

Zeolites used were ZSM-5 zeolite (MFI, HSZ-822HOA, Tosoh Corp., SiO_2/Al_2O_3 (mol/mol) 24, $Na_2O > 0.01\%$, mean particle size (MPS) less than 5 μm), β-zeolite (HSZ-940HOA, Tosoh Corp., SiO_2/Al_2O_3 (mol/mol) 37, Na_2O 0.1 wt%, crystal size 0.05 μm, MPS 5 μm, cation type H^+), Y-zeolite (The reference catalyst of the Catalysis Society of Japan, JRC-Z-HY5.5: $SiO_2/Al_2O_3 = 5.5$, Tosoh Corp.). Tetraethyl orthosilicate ($Si(OC_2H_5)_4$: TEOS, Wako Pure Chem.) was used as a silica source and aluminum tri-sec-butoxide (ASB, Tokyo Chem. Ind.) as an alumina source, malic acid as an organic template and a catalyst for gelation, deionized water, ethyl alcohol and 2-butanol (Nacalai Tesuque) as solvents. The experimental process to make two-layered catalysts was described elsewhere [4]. A flow chart for the preparation of two-layered catalyst is shown in Fig. S1 as a supplemental material. The way of naming samples is as follows; in the case of 2L-10-ZSM (Z50), 2L represents a two-layered catalyst, following 10 the alumina content wt% in a matrix part, ZSM the type of zeolite used (ZSM = ZSM-5), Z50 in parenthesis 50 wt% of zeolite in the two-layered catalyst. Three samples of two-layered catalysts using ZSM-5, 2L-0-ZSM(Z50), 2L-5-ZSM(Z50) and 2L-10-ZSM(Z50), were prepared. The molar ratio of the raw materials is shown in Table 1.

The preparation method of three-layered catalyst was described elsewhere [21]. A flow chart for the preparation of three-layered catalyst is shown in Fig. S2. Initially the reinforced silica-gel was prepared using reinforcing agent, hexamethyldisiloxane (HMDS) and acetic anhydride (AA) solution at 50 °C for 48 h. The two-layered silica-alumina and the reinforced silica-gel were mixed to be roughly homogeneous and heated at 70 °C in a sealed container for 72 h and in an open container for 24 h, and was calcined at 600 °C for 3 h. The prepared catalyst was then pulverized into 45–75 μm. The molar ratio of the raw materials was TEOS: 2- propanol: H_2O: HMDS = 1:4:16:1, the amount of silica obtained from the reinforced gel was determined by TG-DTA in advance, and the amount of zeolite in a three-layered catalyst was controlled by the amounts of the reinforced gel added and a two-layered catalyst.

The name of a three-layered catalyst is denoted as 3L-2L-10-ZSM (Z50)(Z25). 3L means three-layered catalyst using the gel skeletal reinforcement method with HMDS and AA as the reinforcing agent, and a follow is the name of the two-layered catalyst. The last Z25 in parenthesis means the final total amount of zeolite 25 wt% in the three-layered catalyst.

The mixed catalyst with zeolite (ZSM-5, SiO_2/Al_2O_3 (mol/mol) = 24) and kaolin was prepared using a conventional kneading method. The weight ratio of zeolite: kaolin: alumina-sol (binder, Cataloid AP-1) was 26: 58: 16. Sample name was MAT(Kaolin)Z(Z26).

2.2. Characterization of two-layered and three-layered zeolite containing silica and silica-alumina catalysts

X-ray diffraction (XRD) patterns, N_2 adsorption-desorption and TEM observations were carried out for two- and three-layered zeolite containing silica and silica-alumina catalysts. XRD patterns were measured in order to investigate the crystalline phases in the catalysts using Ultima IV (Rigaku) by Ni-filtered Cu-Kα radiation (λ = 1.54 nm) from 2θ = 10° to 70°. Specific surface area, pore volume and pore size distribution were explored by N_2 adsorption and desorption technique using Belsorp Mini II (BEL Japan, Inc.). TEM observations were performed by JEM-1101 (JEOL Ltd.) for digital TEM images. Detailed characterization method was described elsewhere [21].

Table 1
Molar ratio of reagents for ZSM-5 containing two-layered catalysts.

Sample name	Molar ratio					
	TEOS	Malic Acid	ASB	EtOH	2-BuOH	H_2O
2L-0-ZSM(Z50)	1	1.22	0	5	5	10
2L-5-ZSM(Z50)	1	1.22	0.062	5	5	10
2L-10-ZSM(Z50)	1	1.22	0.132	5	5	10

2.3. Catalytic cracking of soybean oil using Curie point pyrolyzer

The component of soybean oil was hydrogen: 10.95 wt%, carbon: 76.64 wt% and nitrogen: 0.30 wt%. 0.20 mg of soybean oil and 1.50 mg of a catalyst were placed in ferromagnetic foil (pyrofoil F500) and were reacted in CPP (Japan Analytical Industry Co., Ltd.: JCI-22). Details of CPP was described in the previous paper [21]. Simple illustration of CPP is shown in Fig. S3. The experimental conditions are as follows: Reaction time was 5 sec, reaction temperature 500 °C. He gas (0.45 MPa) was used as an injection gas. All the products in the gasoline fraction were identified by GC-Flame ionization detector (FID) (GC-2010, Shimadzu Co. Ltd.) with referring to JISK 2536-2 under the conditions, injection temperature 250 °C, detector temperature 320 °C, inlet pressure 100 kPa, column flow rate 0.83 ml/min, a linear velocity of 17 cm/sec, the total flow rate 171 ml/min, split ratio 200, capillary column BP-1, length 60 m, column inner diameter 0.25 mm, column thickness 0.50 μm, column initial temperature 0 °C, holding time 16 min, heating rate 2 °C/min, and final temperature 228 °C. The cracking tests were repeated for one catalyst until the conversions came within a few%.

The conversion of soybean oil was estimated on the basis of Eq. (1) by comparing the total area of the products with those of a standard gas, including C1-C4 (GL Science Co. Ltd., Tokyo, Japan) and toluene.

Conversion (%) = 100 × (Total weight of carbon in products, g)/(Weight of carbon in feed soybean oil, g) (1)

Total weight of carbon in products = (Total areas of products in GC-FID) × (Total weight of carbon in the standard gas)/(Total areas of the standard gas in GC-FID) (2)

Weight of carbon in feed soybean oil was calculated on the basis of elemental analysis data.

Selectivity of a fraction (%) = 100 × (Total weight of carbon in the fraction, g)/(Total weight of carbon in products, g) (3)

Yield of a fraction (%) = (Conversion, %) × (Selectivity of the fraction, %)/100 (4)

3. Results and discussion

3.1. Characterization of ZSM-5-containing two-layered and three-layered silica and silica-aluminas

N_2 adsorption and desorption isotherms of ZSM-5-containing two-layered and three-layered silica and silica-aluminas shown in supplemental materials, Figs. S4 and S5, were assigned to type IV hysteresis due to the formation of mesopore. In the three layered 3L-2L-0-ZSM (Z50)(Z25), 3L-2L-5-ZSM(Z50)(Z25) and 3L-2L-10-ZSM(Z50)(Z25), the stepwise adsorptions were observed at large relative pressure over $P/P_0 = 0.8$, indicating that two types of mesopores would exist, which led to three-layered structure of catalysts. BJH mesopore distributions for zeolite containing layered catalysts are shown in Fig. 1 with that of a mixed catalyst with ZSM-5 and kaolin. Few mesopores existed in the mixed catalyst. In contrast, clear peaks were observed at 4–8 nm for two-layered catalysts. 3.72 nm peaks were detected in 2L-5-ZSM(Z50)

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