Catalytic cracking reaction of vacuum gas oil and atmospheric residue by zeolite-containing microporous and mesoporous composites using Curie point pyrolyzer

Thanita Sonthisawate, Takehiro Nakanishi, Hiroyuki Nasu, Tadanori Hashimoto, Atsushi Ishihara *

Division of Chemistry for Materials, Graduate School of Engineering, Mie University, 1577 Kurima Machiya-Cho, Tsu City, Mie Prefecture 514-8507, Japan

ARTICLE INFO

ABSTRACT

Silica-aluminas with very large mesopores were prepared by the gel skeletal reinforcement technique and were combined with microporous zeolite, resulting in the formation of catalysts with hierarchical structure. Catalytic cracking of vacuum gas oil (VGO) and atmospheric residue (AR), specifically the influence of the pore size of the catalysts on the reactivity of VGO and AR, was investigated using a Curie point pyrolyzer, as a new evaluation technique. Comparing the catalytic cracking of VGO with that of AR, the selectivity for gas products in AR cracking was higher than that in VGO cracking, indicating that dealkylation of aromatic components proceeded. With respect to cracking of VGO the conversion was improved due to the increase in diffusion rate of raw materials with increasing pore size for both β and Y zeolite-containing catalysts. In contrast to the reaction of VGO, the remarkable dependence was hardly observed between conversion and pore size in the cracking of AR presumably because AR, which contained large amounts of heavy fractions with higher boiling point than 500 °C, was difficult to diffuse even in the inside of large pores.

Regarding on the type of zeolite included, more than 70% gasoline selectivity from both VGO and AR was obtained by Y zeolite-containing catalysts. In contrast to this, the gasoline selectivity of about 60% from VGO cracking and 50% from AR cracking, was observed for β zeolite containing catalysts. These results suggested that so-called "supercage", which is included in the inside of the micropores of Y zeolite, would be rather larger than a similar cage of β zeolite which induced higher gasoline selectivity for Y zeolite-containing catalysts.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Catalysts for fluid catalytic cracking (FCC) are composites consisting of zeolite, for example Y zeolite and USY zeolite, and matrix, for instance silica, alumina and silica-alumina [1–3]. Since crude heavy oils, like residue, contain high amount of large hydrocarbons, catalytic cracking is difficult to take place because of the limitation in diffusion into the inside of small pores of zeolite [1–7]. Therefore, matrices with large pores and with catalytic activities should extensively be focused. There were some papers studying on improving catalytic functionality in FCC catalysts, however they were mainly concerned with zeolites [8–12]. The recent advantages in FCC catalysts, however, are mainly derived from the matrix rather than zeolite. Matrix has catalytic activity by itself and tremendously affects the total activity and selectivity as well. Further, the introduction of matrix would give cracking catalysts the following advantages [1–7]; (1) moderating too strong activity of zeolites (reducing the concentration of acid sites), (2) stabilizing against heat and steam as well as mechanical attrition (increasing mechanical strength and friction resistance of catalyst particles), (3) providing

important bulk properties for heat transfer required to maintain proper temperature during regeneration of catalysts and cracking reaction by catalysts in large scale FCC, (4) affecting the diffusion of reactants into the inside of catalyst pores and increasing the cracking activity, that is having advantages to diffuse large size molecules into large size pore.

In order to explore the influence of matrix, we have developed the gel skeletal reinforcement (GSR) technique [13–15], which was developed from traditional sol–gel technique [16–23], to prepare silica and silica-alumina matrix with very large pores. Silica with large mesopores such as 30 nm of pore diameter and 5 cm³/g of pore volume was successfully prepared even after calcination at 600 °C for 3 h. In our technique, the precursor gel was made under the almost ambient conditions where solvent-exchanged silica gel was reinforced by silicone alkoxide compounds such as tetraethylorthosilicate (TEOS) before the calcination. Zeolites were mixed to the matrix described above, and used as catalysts for catalytic cracking of dodecane. As a result, significant influences of the pore structure of the matrix on activity and selectivity for products were observed. On the other hand, we have reported that the Curie point pyrolyzer (CPP) method was quite useful as a convenient simple technique to evaluate catalytic cracking of vacuum gas oil (VGO) [24–26] and fats [27], resources of the heavy hydrocarbons. CPP is a pyrolyzer using pulse heating method by induced heating

---

* Corresponding author.

applying Curie point of ferromagnetic materials, and has the following characteristics; (1) rapid heating (0.2 s) and good repeatability (± 1 °C), (2) disturbing secondary reaction by removing first reaction products produced by ferromagnetic heat source at low atmospheric temperature immediately, (3) capability to analyze small amount of samples. Generally, micro-activity test (MAT) was applied in these cases [28–30], but CPP allows the experiment in short time and conveniently.

This paper reports that the preparation of composite catalysts of zeolites and silica-alumina matrix with large mesopores produced by the GSR technique described above, and that catalytic cracking of VGO and atmospheric residue (AR) as important heavy oil resources was examined by CPP using those catalysts. The report concentrates the influence of matrix on the activity and selectivity by CPP and explores the reactivity of VGO and AR having different boiling range and the reactivity of β and Y zeolite with different micropores.

2. Experimental

2.1. The preparation of TEOS reinforced silica gel

To the preparation of gel was used commercial and analytical grade of tetraethylorthosilicate (Si(OC$_2$H$_5$)$_4$, TEOS; Nacalai Tesque, Inc.) as a starting material, 2-propanol (CH$_3$CH(OH)CH$_3$; Nacalai Tesque, Inc.) as a solvent, 35 wt.% hydrochloric acid (HCl; Nacalai Tesque, Inc.) which was diluted into 0.10 wt.% HCl as acid catalyst, 28 wt.% ammonia solution (NH$_3$ aq.; Nacalai Tesque, Inc.) which was diluted into 2.5 wt.% as controlling agent of pH and deionized H$_2$O as agent for enhancing hydrolysis. Detailed procedure appears in the previous literature [13–15].

A typical preparation method of reinforced silica can be stated as follows: At first, 16.65 g of TEOS mixed with 19.06 g of 2-propanol and dropped 23.24 g of HCl while stirring and stirred for 30 min. Then, NH$_3$ aq. was dropped during stirring to adjust pH to 5. Subsequently, the solution was warmed at 50 °C in oil bath until gelation took place, and aged at 50 °C for 5 h. Then, crushed gel to some extent was immersed in water to enhance hydrolyzing for 24 h. The derived gel was well crushed into fine pieces (less than 5 mm), and exchanged water solvent with 2-propanol for 5 min for 5 times. To improve the yield, pipet was used to eliminate solvent. After the exchanging solvent, the gel pieces were placed into sealed container and 80% TEOS with 20% 2-propanol solution was added to reinforce the frame structure at 50 °C for 48 h. In this experiment, in order to obtain silica-aluminas with different pore sizes, the amount of reinforced TEOS solution was varied by 0, 100, and 200 against the starting material TEOS. The solvent of the derived pieces was exchanged by the same method described above and dried in the sealed container at 70 °C for 72 h. After drying, the obtained gel pieces were heat-treated in flow rate of dry air 600 cm^3/min at heating rate 2.5 °C/min to 600 °C and were kept for 3 h.

The sample name of reinforced silica starts from the degree of the reinforcement and follows by S which stands for silica. The degree of the reinforcement is described below.

$$\text{Degree of the reinforcement} = 100 \times \frac{\text{Reinforced TEOS weight}}{\text{Starting material TEOS weight}}.$$
(1)

For instance, when 16.56 g was the starting material TEOS weight and 33.12 g was the weight for reinforcing 80% TEOS, then $100(33.12) / (16.56) = 200$ wt.%, was expressed as 200S.

2.2. The impregnation of aluminum tri-sec-butoxide: the preparation of silica-alumina

Silica-alumina was produced from reinforced silica, aluminum tri-*sec*-butoxide (ASB; Tokyo Chemical Industry Co., Ltd.) and 2-butanol (Nacalai Tesque, Inc.) as a solvent by the conventional impregnation method [13–15].

The preparation sequence was as follows: 1.014 g of ASB and 28.97 g of 2-butanol were mixed and stirred for 30 min and 4 g of silica was added. After lightly mixing by plastic spatula, the mixture was sealed and aged at room temperature for 24 h. Then samples were dried at 100 °C oil bath in open system to eliminate solvent and then heat-treated as the same condition for silica. 5 wt.% to whole weight was alumina impregnated in whole samples. The samples containing alumina were expressed by adding A at the end of silica sample name, as 200SA.

2.3. Preparation of mixed catalysts with zeolite

In order to prepare mixed catalysts with zeolite, 58 wt.% of silica-alumina produced by impregnation technique, 26 wt.% of β zeolite (HSZ-940HOA; SiO$_2$/Al$_2$O$_3$ 37 mol/mol, Tosoh Corp.) or Y zeolite (JRC-HY5.5; SiO$_2$/Al$_2$O$_3$ 5.5 mol/mol, reference catalyst of Catalysis Society of Japan, Tosoh Corp.) and 16 wt.% (as Al$_2$O$_3$) of alumina sol (Cataloid AP-1, Shokubai Kasei Kogyo Co., Ltd.) used as binder, were mixed and kneaded with adding 2-propanol. After the mixture had enough viscosity, the substances were mold-pressed by cylindrical sodium press (NP-1, Sanki Seisakusho Co., Ltd.) and were heat-treated under the same condition as others (600 °C for 3 h). The sample name is denoted as MAT(type of silica-alumina)-(type of zeolite), for example, MAT(0SA)-β.

2.4. Characterization of catalyst samples

2.4.1. N$_2$ adsorption and desorption measurement
In order to measure specific surface area, pore volume and pore size distribution, the adsorption experiment of N$_2$ was carried out. As pretreatment, samples were placed at 350 °C in vacuum for 3 h using BELPREP II (BEL Japan, Inc.). Then isothermal curves of N$_2$ adsorption at 77 K were plotted by BELSORP-mini-I (BEL Japan, Inc.). Data obtained using BET method for specific surface area and BJH methods for mesopores were analyzed by BELMaster (BEL Japan, Inc.) according to ISO 9277 and JIS Z 8830 specification.

2.4.2. X-ray diffraction patterns
X-ray diffraction (XRD) patterns were explored to know the crystal structure of derived samples by Ultima IV (Rigaku Corp.). Pulverized samples were set on the glass holder fixed to the holder inside machine chamber. X-ray source was nickel-filtered Cu-Kα X-ray source radiation ($\lambda = 1.5405$ nm) with 40 kV and 100 mA of applied voltage and current under the following measuring conditions: scan mode CONTINUOUS, slit (SS) 1° (DS) 1° (RS) 0.3 mm, present time 1 s, scan speed of 2°/min and scan range from $2\theta = 10$–70°.

2.4.3. Adsorption and desorption of NH$_3$
Adsorption and desorption of NH$_3$ were investigated to observe the acidity of the catalysts obtained by ammonia-pulse method. First of all, the 40 mg of samples was packed in the middle of quartz wool inside the reactor, and was heated up to 600 °C with 10 °C/min under 30 cm^3/min of He atmosphere and kept for 3 h. Then, the temperature of catalysts was cooled down to 100 °C and 1.0 cm^3/pulse of NH$_3$ for the adsorption was introduced until the area reached that of one pulse. Next, N$_2$ was continuously introduced into the system to remove unnecessary NH$_3$ for 30 min. Subsequently, catalysts adsorbing NH$_3$ were heated again to 650 °C to desorb NH$_3$. The NH$_3$ gas was detected and quantified by gas chromatography-thermal conductivity detector (GC-TCD, GC-8A, Shimadzu Corp.). The measuring condition was as follows; INJ/DET 170 °C; COL 140 °C; ATTN 16; Current 100 mA; column flow 50 cm^3/min.