



Upgrading of light cycle oil via coupled hydrogenation and ring-opening over NiW/Al₂O₃-USY catalysts

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ABSTRACT

A series of ultrastable Y (USY) zeolite samples with different acidities and pore sizes are prepared via hydrothermal and acid treatments. NiW sulfide catalysts are maintained on a mixed support of USY zeolite and Al₂O₃. The catalytic coupled hydrogenation and ring-opening performance are studied on a continuous fixed-bed reactor using tetralin as the model compound. All catalysts show high tetralin conversions under the reaction conditions studied [$T=613\text{ K}$, $P=4.0\text{ MPa}$, $LHSV=2.0\text{ h}^{-1}$, $H_2/\text{oil (v/v)}=500$]. Product yields and selectivity are mainly determined by the zeolite property (i.e., acidity). A medium to strong zeolite acidity is the key factor in the ring-opening selectivity of tetralin. A maximum high cetane ring-opening product yield of 39.1 wt% is obtained at a C₁₀ yield of 98.2 wt% for a USY zeolite with medium acidity. Using an fluid catalytic cracking light cycle oil feedstock, the activity of the catalyst is higher than that of commercial catalysts, giving a 14-unit cetane number increase at a diesel yield of 97.6 wt%. Because the first step of the ring-opening reaction is hydrogenation, the catalyst must have high hydrogenation activity. The WS₂ slabs have a high average layer number of 2.7 on the catalyst using the support presented here.

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1. Introduction

Light cycle oil (LCO) from fluid catalytic cracking (FCC) is becoming an important source for diesel pools. It is characterized by a high polyaromatic content and low cetane number. Several approaches have been proposed to improve the cetane number, including the use of cetane boosters [1], blending with Fischer–Tropsch gas-to-liquid diesel fuels [2], deep hydrotreating [3], hydrocracking [4], and selective ring-opening (SRO) [5]. In contrast to conventional hydrocracking, selective ring-opening requires that only one C–C bond in the naphthenic molecule be broken, thus preventing significant molecular weight reduction of the feed.

Selective ring-opening can be carried out on certain noble metals by hydrogenolysis. The hydrogenolysis ability of these catalysts increases in the order of: Pt < Rh < Ir < Ru [6–8]. The ring-opening of naphthenes can also take place through an acid-catalyzed process performed primarily on zeolites. The activity is reportedly dependent on the number and strength of Brønsted acid sites and porosity of the support [9,10]. Thus, the best ring-opening results are obtained from zeolites exhibiting medium acidity. The use of zeolites with large pores favors the ring-opening reaction [11–13].

Ring-opening reactions are enhanced by the use of bifunctional catalysts [14]. The judicious control of the metal to acid ratio in a given catalyst is important. The formation of the ring-opening products increases with increasing proximity between Pt and the acid sites [15]. Thus, a close relationship between the metal and acid sites is necessary for improvement of bifunctional catalysts in the ring-opening reaction.

Numerous studies have been conducted on the use of noble metal catalysts, but they are costly and easily poisoned by sulfur compounds [15–17]. These catalysts have to be used in a multi-stage process. Metal sulfide catalysts are able to catalyze the ring-opening reaction in the presence of sulfur compounds. However, few studies have focused on these materials. In this paper, we investigate the use of mixed ultrastable Y (USY) zeolite and Al₂O₃ to support sulfided NiW-based catalysts for the hydrogenation and ring-opening of tetralin and the hydrotreatment of LCO. The influences of the acidity and pore size of USY zeolite are also studied. The correlations between the catalytic activity and structures of NiW sulfide on the support are further investigated.

2. Experimental

The USY zeolite was prepared from the starting NaY sample by ammonium exchange, followed by subsequent hydrothermal and acid treatment. By changing the treatment conditions, three

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kinds of USY samples were obtained. The support was prepared by mixing zeolite and pseudo-boehmite. The resulting compound was extruded to form a cylindrical extrudate, which was dried overnight at 383 K and then calcined in the air at 823 K for 4 h. The composite support obtained was designated as AUSY. NiW catalysts with a load of 4 wt% NiO and 27 wt% WO₃ were prepared via the pore volume co-impregnation method with an aqueous solution of ammonium metatungstate and nickel nitrate. The catalyst was dried overnight at 393 K and calcined at 753 K for 4 h. As a reference catalyst without zeolite, an Al₂O₃-supported NiW catalyst with the same NiO and WO₃ loads was prepared.

X-ray diffraction (XRD) patterns were recorded on a Shimadzu-6000 diffractometer using Cu K α radiation at 40 kV and 30 mA. The porosity of each sample was determined by measuring the N₂ isotherm at 77 K with a Micromeritics ASAP 2020 automated system. The total surface area was calculated according to the BET isothermal equation, and the micropore volume, the mesopore volume, and external surface area were evaluated by the *t*-plot method. The pore size distribution profile was calculated using the BJH method with an N₂ desorption isotherm. Ammonia-temperature-programmed desorption (NH₃-TPD) of the zeolites was performed using Quantachrome Autosorb-1 equipped with a thermal conductivity detector (TCD) to monitor the exit gas. The morphology of the NiW sulfide was observed by high resolution transmission electron microscopy (HRTEM) on a Tecnai G² F20 field emission machine operated at 200 kV. Samples were prepared by the drop method.

The coupled hydrogenation and ring-opening of tetralin was evaluated in a continuous flow fixed-bed micro-reactor under the following conditions: a model feed of 10 wt% tetralin in decane, a catalyst load of 1.0 g, a reaction pressure of 4.0 MPa, a reaction temperature of 613 K, a feed flow rate of 3.62 mL/h, and an H₂/oil ratio of 500 (v/v). The catalysts were first pre-sulfided in situ with a sulfiding feed of 10 vol% CS₂ in decane at 4.0 MPa and 603 K for 4 h. After steady-state conditions were reached, the liquid effluents were periodically collected and measured on an SP 3420 gas chromatograph (GC) using a flame ionization detector and a DM-5 capillary column (30.0 m \times 0.25 mm \times 0.32 μ m). Identification of the reaction products was accomplished by mass spectrometry (MS) and by a comparison of the retention times with those of available standard mixtures. The GC patterns obtained from our study were compared with those in Sato's work [18]. To facilitate the discussion, reaction products were grouped as follows: (a) light paraffins, composed mainly of propane and isobutene; (b) light naphthenes with less than 10 carbon atoms; (c) decalin; (d) decalin isomers or isodecalins having one or two C₅ naphthenic rings; and (e) ring-opening products, composed mainly of *n*-butylbenzene and *iso*-butylbenzene having the same number of carbon atoms as the aromatic reactant (C₁₀). These are the most important products from the point of view of cetane number.

The hydrotreatment of the catalysts was conducted in a 20 mL continuous flow fixed-bed reactor using Daqing FCC LCO as the feed. The length of the catalyst was 2–3 mm, and the catalyst loading volume was 20 mL. The catalysts were first pre-sulfided in situ with a sulfiding feed of 2 wt% CS₂ in kerosene. The reaction operating conditions were 8.0 MPa, 633 K, an LHSV of 1 h⁻¹, and an H₂/oil ratio of 800 (v/v). The reaction products were condensed and periodically

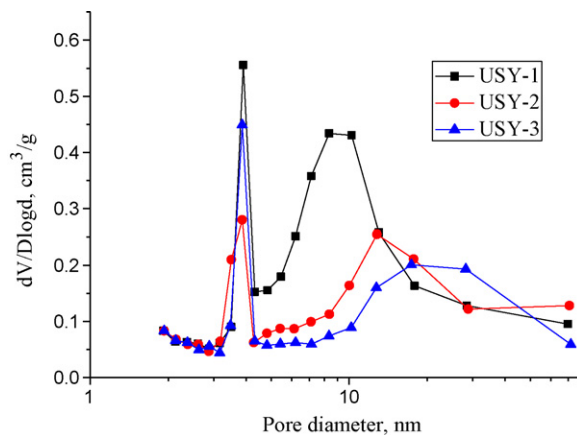


Fig. 1. Pore size distribution of the zeolites.

separated from a gas-liquid separator. After the feedstocks were treated for about 5 days, the liquid products were collected and analyzed. The diesel cut boiling range was found to be 453–633 K. The nitrogen and sulfur contents in the samples were analyzed according to ASTM D4629 and ASTM D4294, respectively. The total aromatic content was determined by the standard fluorescence indicator adsorption (FIA). The cetane number was determined via diesel engine testing.

3. Results and discussion

3.1. Characterization of zeolites

The textural properties of the zeolites determined by N₂ adsorption are shown in Table 1.

The BET surface area (S_{BET}) increases in the order of: USY-1 < USY-2 < USY-3. The same trends can be observed for the micropore surface area (S_{micro}), total pore volume (V_p), and micropore volume (V_{micro}) of the zeolites. The results clearly show that the micropore properties of USY-3 are preserved well. The external surface area (S_{exter}) and the mesopore volume (V_{meso}) of USY-3 are also the highest obtained. Sato et al. claimed that mesopore structures can influence the interaction between zeolite and NiW sulfide and the catalytic performance of the USY-based hydrocracking catalyst [19]. As such, precise control of the mesopore structures is required. USY-1 has the largest average pore diameter (D_{aver}).

Fig. 1 shows the pore size distribution profiles of the zeolites. All USY zeolites have two peaks at about 3.8 and 15 nm. The former is related to the mesoporosity created during the dealumination procedure used to obtain high-silica faujasites [20], while the latter is attributed to the void spaces among the particle agglomerates. The intensity of the peaks at about 3.8 nm decreases in the order of: USY-1 > USY-3 > USY-2.

Fig. 2 shows the NH₃-TPD profiles of the zeolites. The TPD profile of USY shows a single peak at about 460 K. The peak areas of the NH₃-TPD curves decrease in the order of: USY-3 > USY-2 > USY-1. The use of zeolites with medium acidity favors ring-opening reactions [9].

Table 1
Textural properties of the zeolites.

Sample	S_{BET} (m ² /g)	S_{micro} (m ² /g)	S_{exter} (m ² /g)	V_p (cm ³ /g)	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)	D_{aver} (nm)
USY-1	396	306	90	0.38	0.16	0.22	3.88
USY-2	595	531	64	0.45	0.27	0.18	3.05
USY-3	731	605	126	0.61	0.29	0.32	3.32

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