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Catalyst design and development for upgrading aromatic hydrocarbons

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Abstract

Background and strategy of catalyst development for upgrading aromatic hydrocarbons are intensively discussed. Originally prepared catalysts (hydrogenation and hydrocracking catalysts) were used for accelerated aging tests. Though each catalyst showed superior catalytic performance as compared to commercially available catalysts, a severe deactivation was observed on the hydrocracking (HC) catalysts. A new type of HC catalyst was designed and prepared, based on the understanding of catalyst deactivation. High silica NaY zeolites were synthesized using crown-ether. USY zeolites were then prepared by ion exchange, steaming and calcining. Surface properties and catalytic functions of well-crystallized USY zeolites were investigated to develop practical HC catalysts. The Ni–W catalyst prepared using the newly prepared USY zeolite showed a considerable improvement in the HC activity. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Clean fuel production; Hydrogenation (HY) catalysts; Hydrocracking (HC) catalysts; Y zeolites

1. Background

Asian Pacific demands of petroleum products are increasing remarkably due to the rapid growth of the local economies. There is a strong need to produce fuels from conventional and synthetic crudes, because consumption of transportation fuels is increasing continuously, while heavy oil consumption is decreasing gradually. Since the reserves of conventional crudes are declining, feed stocks of heavy hydrocarbons have to be converted into lower boiling point products in greater yields and with more selectivity. After the oil crisis in 1978, lots of research and development have been done to produce transportation fuels from heavy hydrocarbons [1].

On the other hand the regulations governing hetero-atoms and aromatic content in fuels are becoming increasingly severe to minimize air pollution such as NO_x and particulates emitted from motor vehicles [2]. Although research and development of exhaust gas treatment and combustion control have been carried out, practical processes and catalysts are not yet developed, resulting in severe regulations for aromatics and hetero-atoms in fuels.

Until recently, most regulations on diesel fuel were only concerned with sulfur content. Now, reduction of aromatic content is also required since aromatics contribute significantly to the formation of particulate emissions in exhaust gases. As the result of the

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tightening of the regulations, there is now great interest in the research and development of processes and suitable catalysts for hetero-atom removal and aromatic reduction in middle distillates [3–5].

2. Strategy of catalyst development

These trends clearly show that clean transportation fuels with lower amounts of hetero-atoms and aromatics have to be produced from unconventional feed stocks. For producing lighter fractions from heavy hydrocarbons, three kinds of approaches (thermal cracking, RFCC and hydrocracking) are practically applied, as described in Fig. 1. Thermal cracking processes are popular in USA and EU, though fuel quality is rather poor. RFCC routes are commonly used in Japan to meet product demands and Japanese regulations.

The hydrocracking route will become more important in near future for producing higher quality fuels. Since heavy hydrocarbons contain larger amounts of aromatics and hetero-atoms, hydrocracking does not proceed without aromatic hydrogenation and hetero-atom reduction. This means that both hydrogenation (HY) and hydrocracking (HC) catalysts with superior catalytic performance are required to develop a practical hydrocracking process.

HY and HC catalysts were designed and prepared based on fundamental studies such as surface properties of catalysts or nature of HY and HC active sites [6]. After evaluating catalytic functions by model test reactions, originally prepared catalysts were applied to upgrading of feed stocks. Accelerated aging tests were then carried out to clarify catalyst performance. Long-time life tests were done by a petroleum refining company. Our flow diagram of catalyst research for developing hydrotreating catalysts is illustrated in Fig. 2. During model tests, upgrading and life tests, surface properties of the catalysts were fully characterized.

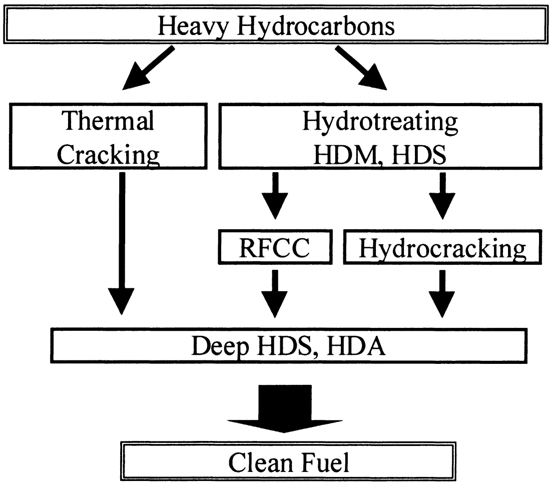

Fig. 1. Clean fuel production from heavy hydrocarbons.

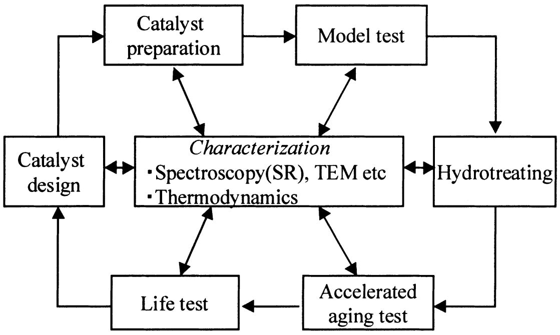

Fig. 2. Research flow diagram of hydrotreating catalysts.

3. Catalytic performance of HY and HC catalysts

Ni–Mo and Ni–W/Al_2O_3 catalysts were designed and developed for the HY catalysts. In the course of research and development of the HY catalysts, metal loading and properties of the support were optimized to give the highest initial HY activity [6]. A commercially available NaY zeolite (silica/alumina ratio=5) was used for preparing the ultra stable Y (USY) zeolite of the HC catalyst. Ni–W/USY–Al_2O_3 (60% USY and 40% Al_2O_3) catalyst was designed and prepared for the HC catalysts. A life test of the HY catalysts was then carried out using polyaromatic feed stocks (coal-derived gas oil), followed by a life test of the HC catalysts using hydrogenated polyaromatics.

Based on the understanding of catalyst deactivation behavior observed on the HY and HC catalysts, catalytic performance of each catalyst was improved by minimizing carbonaceous deposits, crystal growth of WS_2-like structures and segregation of Ni from W

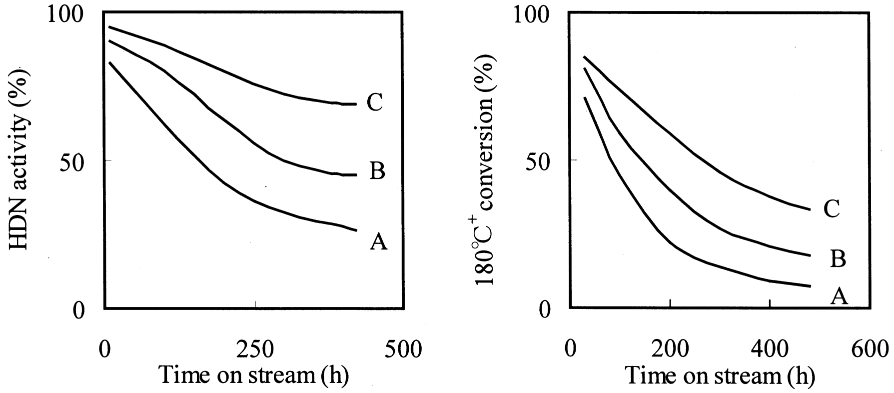

Fig. 3. Catalyst performance of hydrogenation and hydrocracking catalysts. (a) HDN activities of HY catalysts (Ni–W/Al_2O_3) during accelerated aging tests. (b) HC activities of HC catalysts (Ni–W/USY–Al_2O_3) during accelerated aging tests. Cat. A, reference catalyst; Cat. B, originally developed catalyst; Cat. C, improved catalyst. Reaction conditions were as follows: H_2 pressure, 6.9 MPa; reaction temperature, 370°C; LHSV, 2 h^{-1}; H_2/oil, 1000 Nm^3/l. For the accelerated aging tests of HY reactions, quinoline was added into the coal-derived gas oil, while the product obtained after first-stage upgrading over the HY catalyst (hydrogenated coal-derived gas oil) was used as the feed of HC reactions.

during HY or HC reaction. Fig. 3 shows catalytic deactivation behavior of the HY and HC catalysts during accelerated aging tests. The improved HY catalyst showed much higher catalytic performance for a hydrodenitrogenation of the feed as compared to a reference HY catalyst, which was selected among commercially available catalysts because of having the highest catalytic performance. Large improvements in the HC activity (180°C^+ conversion in the gas oil) and deactivation were also observed on the improved HC catalysts. However, the HC activity of the Y zeolite catalyst decreased to a large extent after the accelerated aging test, while much less deactivation was observed on the improved HY catalyst. These results clearly show that a new generation of HC catalyst with a long life is required to establish a practical upgrading process of aromatic hydrocarbons.

4. Design concept of the new hydrocracking catalyst

Concerning the carbonaceous deposits, the crystal growth of WS_2-like structures and the segregation of Ni from W, similar behavior was observed on the HY and HC catalysts which were used for the accelerated aging tests. Typical different behavior measured on the aged HC catalyst is the adsorption of nitrogen-containing compounds and NH_3 onto the acid sites of the catalyst. When comparing the deactivation behavior of the HC catalyst with that of the HY catalyst, the severe reduction of the HC activity will be mainly due to the adsorption of nitrogen-containing compounds and NH_3 onto the acid sites. In fact, other accelerated aging tests revealed that the HC activity of the improved HC catalyst decreased with the increase of nitogen-containing compounds in feed stocks, though the deactivation behavior was somewhat influenced by the type of nitogen-containing compound (Fig. 4).

These results indicate that a highly active HC catalyst, which is tolerant to the nitrogen-containing compounds, has to be developed for establishing a practical HC process of aromatic hydrocarbons. Although various kinds of zeolites and double oxides have been prepared and investigated, Y zeolites show the highest catalytic performance for a ring-opening reaction of hydrogenated aromatic rings among various zeolites and double oxides so far developed. Accordingly researches related to the preparation and modification of Y zeolites will be most effective for developing a practical HC catalyst with a superior activity and long life.

Since HC activity of Y zeolite comes from the crystalline structure, the well-crystallized structure must be effective for increasing the HC activity. It is well known that the HC activity is somewhat influenced by the acidity of zeolite, whereas the

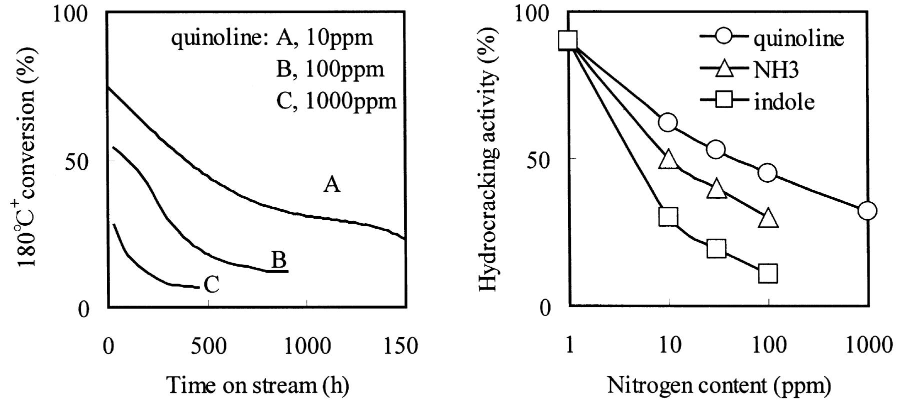

Fig. 4. Deactivation of the hydrocracking catalyst (Ni–W/USY–Al_2O_3). (a) Accelerated aging tests of the hydrocracking catalyst. HC reaction conditions are the same as described in Fig. 3. Quinoline (10, 100 and 1000 ppm) was added into the feed of the HC reactions. (b) Deactivation behavior of the hydrocracking catalyst. HC activities were measured by model test reactions using batch type microreactors (50 cm^3). Diphenylmethane was used as a model compound. The HC activity was evaluated by total yields of benzene and toluene. Reaction conditions of batch reactors were as follows: H_2 initial pressure, 6.9 MPa; reaction temperature, 400°C; reaction time, 1 h; catalyst, 0.3 g; diphenylmethane, 10 ml.

relationship between the HC activity and the acidity was not clarified. If the HC activity is linearly correlated with the acidity, it will be difficult to develop a HC zeolite catalyst with a long life, because the adsorption of the nitrogen-containing compounds and NH_3 onto the Y zeolite increases with the increase of the acidity. This means that the HC activity has to be enhanced by producing well-crystallized zeolites, while the adsorption of the nitrogen-containing compounds and NH_3 on the HC catalyst has to be minimized by controlling the acidity of the zeolite.

Based on the above consideration we decided to prepare a well-crystallized NaY zeolite with a high framework Si/Al ratio and to modify the NaY zeolite to a hydrophobic USY zeolite. The hydrophobic USY zeolite prepared using the synthesized NaY zeolite (SiO_2/Al_2O_3 ratio=7, NaY7) will possess well-crystallized structures and will give higher HC activity than the USY zeolite obtained from commercially available NaY zeolites (SiO_2/Al_2O_3 ratio=5, NaY5). This USY7 zeolite will maintain higher HC activity for a long time, because the adsorption of the nitrogen-containing compounds and NH_3 on the Y7 zeolite must be successfully reduced to a considerable extent. Since the USY7 zeolite will give higher HC activity, the reaction temperature of hydrocracking will be lowered to some extent. This must be effective for reducing the carbonaceous deposits, the crystal growth and the segregation of Ni, indicating an additional contribution to superior catalyst performance.

5. Preparation of well-crystallized Y zeolites

Fundamental research into the preparation of well-crystallized NaY zeolites with a high framework Si/Al ratio was done for developing well-crystallized USY zeolites with fewer acid sites. NaY zeolites (SiO_2/Al_2O_3 ratio=7, NaY7) were synthesized using hydrogel and crown-ether as template [7]. Sodium aluminate, sodium silicate, sodium hydrate and distilled water were used for the preparation of crystalline seeds. Then faujasite-type zeolites with a high framework Si/Al ratio were synthesized using the hydrogel (2.4 Na_2O; Al_2O_3; 10 SiO_2; 140 H_2O; $C_{10}H_{20}O_5$) consisting of sodium aluminate, sodium silicate, silica-sol, seeds, template and distilled water. As reference zeolites, commercially available NaY zeolites (SiO_2/Al_2O_3 ratio=5, NaY5) were also synthesized, using hydrogel with the following composition: 2.8 Na_2O; Al_2O_3; 8.4 SiO_2; 108 H_2O.

After crystallization at 110°C, zeolites were taken out of autoclaves, followed by washing and drying at 130°C. NH_4^+-forms of the zeolites were obtained by NH_4^+ ion exchange of the NaY5 and NaY7 zeolites in $(NH_4)_2SO_4$ solution. Protonated forms (HY zeolites) were produced after calcination of NH_4^+-forms at 550°C. USY zeolites (USY5 and USY7) were prepared by hydrothermal treatment in order to optimize the acid and hydrophobic properties of the HY zeolite. For preparing USY5 and USY7 zeolites, HY5 and HY7 zeolites, containing 0.2–0.6 wt% of Na_2O, were first made using the ion exchange and calcination of the NaY5 and NaY7 zeolites. Steaming of the HY5 and HY7 zeolites was then carried out at 700–900°C for 1 h. USY5 and USY7 zeolites were used for characterizing chemical and physical properties and for measuring HC activities.

6. Characterization of well-crystallized Y zeolites

Crystalline structures of the newly prepared zeolites were characterized using a scanning electron microscope (SEM) and an X-ray diffractometer (XRD). The relative crystallinity of the Y zeolites was determined by measuring the peak intensities of the XRD pattern. A commercially available Y zeolite was selected as the standard for evaluating the crystallinity of the Y zeolites. Synchrotron radiation excited X-ray photoelectron spectroscopy (SR-XPS), which was designed and developed by the authors for characterizing surface properties of advanced materials [8], was applied for analyzing the depth profile of outer surface layers on Y zeolites. SR-XPS measurements were done at the BL-13C of the Photon Factory in the National Laboratory for High Energy Physics. Acid properties of the zeolites were evaluated using temperature programmed NH_3 desorption (NH_3 TPD).

Cubic or hexagonal crystal forms were clearly observed on the NaY7 zeolites using SEM, while crystal forms were dependent on preparation conditions such as template. No typical crystal form was observed on the NaY5 zeolites probably due to lower crystallinity. In fact, XRD measurements showed that the NaY7 zeolite possesses higher crystallinity than the NaY5 zeolite (Fig. 5). Further XRD measurements revealed that the crystallinity retention of HY7 zeolites was much less than that of HY5 zeolite after the ion exchange and steaming (Table 1). When severe ion exchange conditions were applied to the preparation of HY zeolites, the NaY7 zeolite was much more stable than the NaY5 zeolite. Sodium in the NaY7 zeolite was more easily removed without losing the crystalline structure of the Y7 zeolite as shown in Fig. 6. The crystalline structure of the NaY5 zeolite was collapsed when the sodium content of the zeolite was reduced to the level of 0.02 wt% as Na_2O.

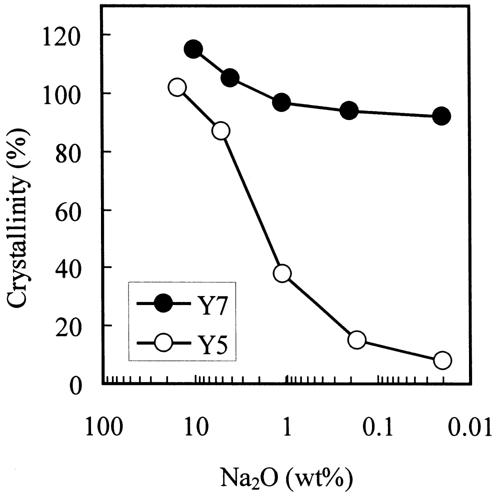

Fig. 5. Crystallinity of Y zeolites after the ion exchange and calcination. A commercially available Y zeolite was used as the standard for evaluating crystallinity. Severe ion exchange conditions were applied.

Table 1
Characteristics of HY5 and HY7 zeolites after steaming at 700°C, 800°C and 900°C

	HY	700°C	800°C	900°C
Y5 zeolite				
Crystallinity (%)	73	58	51	18
Unit cell dimension (Å)	24.66	24.39	24.36	—
SiO_2/Al_2O_3	5.1	15.1	18.3	—
Y7 zeolite				
Crystallinity (%)	100	93	81	27
Unit cell dimension (Å)	24.56	24.42	24.37	24.24
SiO_2/Al_2O_3	7.0	12.2	16.4	—

HY5 and HY7 zeolites containing 0.4 wt% of Na_2O were used for steaming at 700–900°C for 1 h.

The crystal forms were clearly observed using SEM even after steaming HY7 zeolites at 700–900°C, though the smooth crystal surface on the NaY7 zeolite was changed to an uneven surface. Fig. 6 shows the crystallinity retention of Y5 and Y7 zeolites during preparation of USY zeolites. The crystallinity of the Y

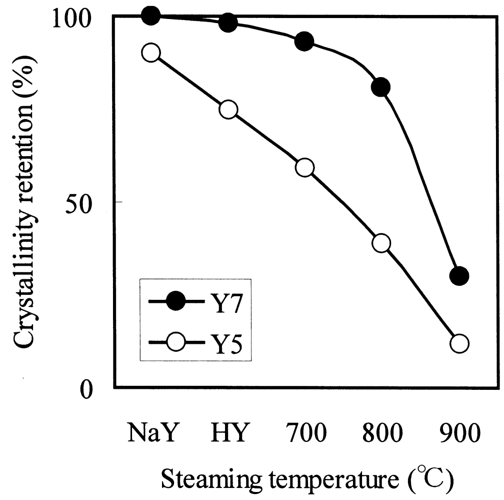

Fig. 6. Crystallinity retention of Y zeolites after steaming. HY5 and HY7 zeolites each containing 0.4 wt% of Na_2O were used for steaming at 700–900°C.

zeolites decreased with increasing of steaming temperature. The HY7 zeolite was much more stable than the HY5 zeolite during USY preparation, suggesting that well-crystallized USY zeolites (USY7) are applicable for the preparation of the HC catalysts.

Since SEM measurements detected the uneven surfaces on the USY zeolites, precise characterization of the Y zeolites was performed using SR-XPS. The attenuation length (Å) of Si2p photoelectrons in NaY zeolites as a function of electron energy (eV) is summarized in Fig. 7. This indicates that a zeolite surface can be characterized more sensitively using a lower exciting energy of X-ray obtained from the synchrotron radiation. Fig. 8 shows depth profiles of Si/Al ratio on the zeolite surface layers before and after the ion exchange and calcination of the NaY5 and NaY7 zeolites. Different exciting energies (246, 388 and 760 eV) of SR X-ray were applied to the surface characterization of the Y zeolites. Surface Al/Si ratios of the NaY5 and NaY7 zeolites were higher than bulk Al/Si ratios of the NaY5 and NaY7 zeolites. The Al/Si ratios decreased with increasing of attenuation length. These results indicate that aluminium was concentrated in outer surface layers of the originally prepared NaY zeolites. When the sodium content was reduced to 0.02 wt% as Na_2O by the severe ion exchange treatment, strange depth profiles were observed on HY5 zeolites. The Al/Si ratios on the HY5 zeolite increased after the ion exchange and calcination, though the Al/Si ratio decreased to some extent with increasing of attenuation length (Fig. 8(a)). Since bulk Al/Si ratio of the HY5 zeolite decreased after the above treatment, the higher Al/Si ratios of the surface layers seem to show the formation of amorphous alumina or silica–alumina. This formation of amorphous aluminum, provably due to the collapse of crystalline structures as already analyzed by XRD, will reduce HC activity of Y zeolite. On the other hand the Al/Si ratio decreased on the HY7 zeolite after the ion exchange and calcination showing that dealumination of the NaY7 zeolites was successfully performed without losing the crystallinity of the Y7 zeolite. This means that amorphous aluminum was not concentrated on the HY7 zeolite surface, though unevenness was observed on the surface by SEM. The well-crystallized HY7 zeolite will give higher HC activity and will reduce the adsorption of carbonaceous deposits and NH_3.

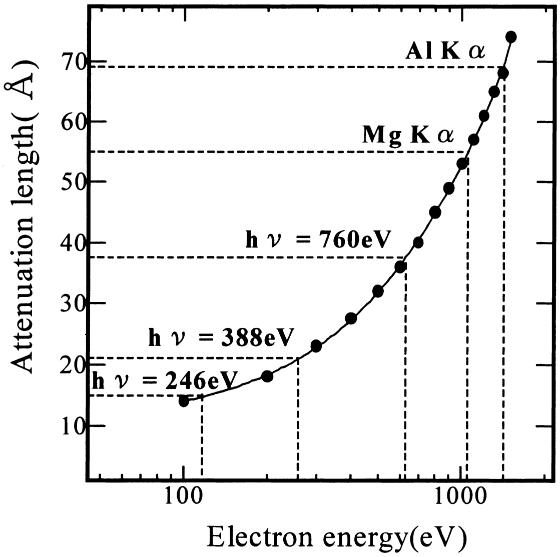

Fig. 7. Attenuation length of Si2p photoelectrons in NaY zeolites as a function of electron energy.

7. Hydrocracking activities of the new zeolite catalysts

HC activities of Y zeolite catalysts were evaluated using model test reactions. Tetralin was used as a

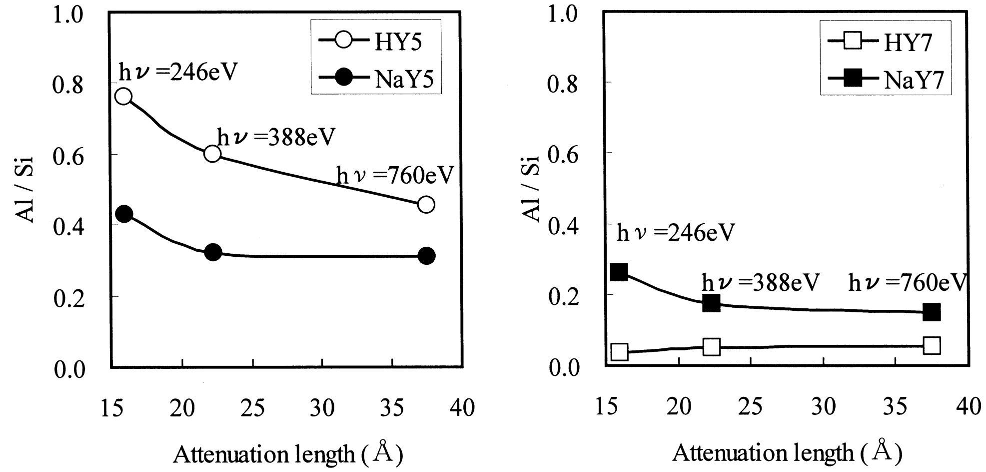

Fig. 8. Depth profile analyses on outer surface layers of Y zeolites. Si2p and Al2p photoelectron spectra, excited by the synchrotron radiation (SR, BL13C) in the PF, were used for measuring Si/Al ratios of Y zeolites. The Si/Al ratios obtained using 246, 388 and 760 eV of SR exciting energies were plotted as a function of the attenuation length. HY5 and HY7 zeolites, each containing 0.02 wt% of Na_2O, were obtained after the ion exchange of NaY5 and NaY7 zeolites.

model compound for measuring the HC activity of the ring-opening reaction, while the HC activity of C–C bond cleavage was determined by the model test reaction of diphenylmethane. The model test reactions were carried out using batch type microreactors ($50\,cm^3$). Fig. 9(a) shows the HC activities of the HY5 and HY7 zeolites after ion exchange and calcination. The HC activity increased with the decrease in sodium content. As expected from the characterization of newly prepared zeolites (Fig. 5), the HY7 zeolites gave higher HC activities than the HY5 zeolites. When a severe ion exchange of NaY5 zeolite was done,

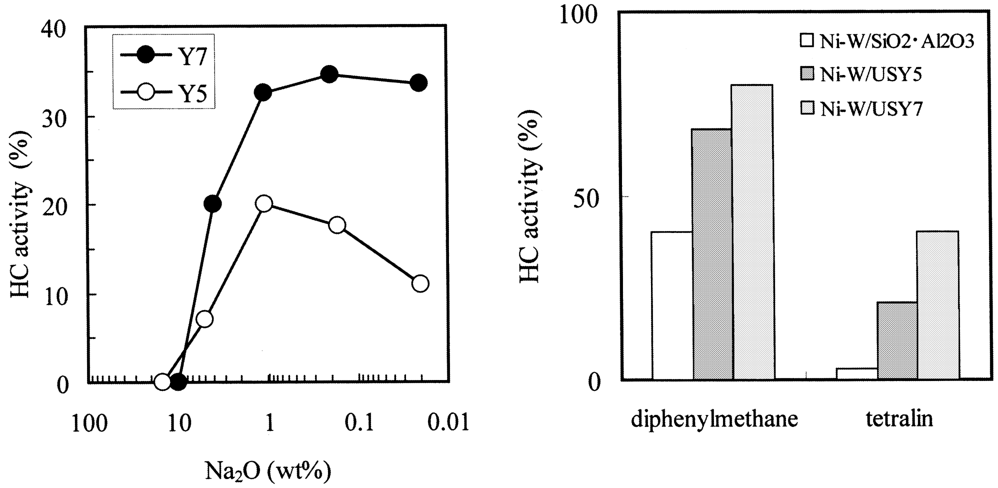

Fig. 9. Hydrocracking activities of new zeolite catalysts. (a) HC activities of HY5 and HY7 zeolites after the ion exchange and calcination. Diphenylmethane was used as the model compound. Reaction conditions were the same as described in Fig. 4(b). (b) HC activities of the new HC catalysts (Ni–W/USY). USY5 and USY7 were used for the preparation of the HC catalysts. A silica–alumina supported catalyst (Ni–W/SiO_2–Al_2O_3) was also prepared as a reference HC catalyst. Diphenylmethane and tetralin were used as the model compounds. Reaction conditions of batch reactors were as follows: H_2 initial pressure, 6.9 MPa; reaction temperature, 375°C; reaction time, 1 h; catalyst, 0.3 g; diphenylmethane (tetralin), 10 ml.

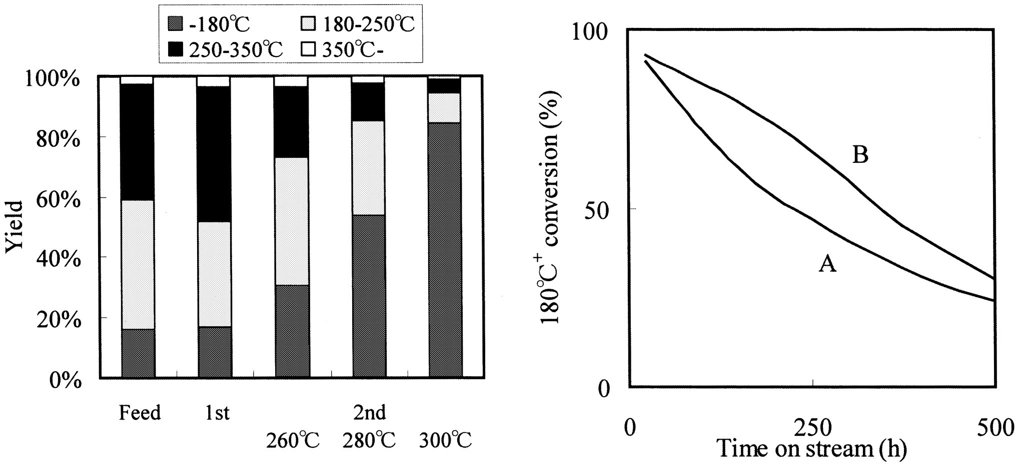

Fig. 10. Catalytic performance of the newly prepared HC catalyst (Ni–W/USY–Al_2O_3). (a) Two-stage upgrading of LCO over the HC catalyst. Ni–Mo/Al_2O_3 catalyst and Ni–W/USY–Al_2O_3 catalyst were used for first- and second-stage upgrading, respectively. Reaction conditions were as follows: H_2 pressure, 6.9 MPa; reaction temperature, HY, 370°C, HC, 260–300°C; LHSV, 2 h^{-1}; H_2/oil, 1000 Nm^3/l; Cat., 15 cm^3. For the HC reactions (second-stage upgrading), the product obtained after first-stage upgrading over the HY catalyst (hydrogenated LCO) was used as the feed. (b) Accelerated aging tests of the HC catalysts. A, originally prepared catalyst; B, newly prepared catalyst. Reaction conditions were as follows: H_2 pressure, 6.9 MPa; reaction temperature, 370°C; LHSV, 2 h^{-1}; H_2/oil, 1000 Nm^3/l; Cat., 15 cm^3. For the accelerated aging tests of HC reactions, the product obtained after first-stage upgrading over the HY catalyst (hydrogenated coal-derived gas oil) was used as the feed.

lower HC activity was obtained because of crystal collapse. As already mentioned, the HC activity was intimately correlated with the crystallinity of Y zeolite, but no simple relationship between the HC activity and the acidity was observed in this work.

Fig. 9(b) shows the HC activities of Ni–W/USY catalysts prepared using the USY5 and USY7 zeolites. A silica–alumina supported catalyst (Ni–W/SiO_2–Al_2O_3) was also prepared as a reference catalyst. In spite of lower amounts of effective surface area and mesopores, the Ni–W zeolite catalysts showed much higher HC activities than the Ni–W/SiO_2–Al_2O_3 catalyst. The highest HC activities for the C–C bond cleavage and ring-opening reactions were obtained on the Y7 zeolite catalyst. The superior HC activity of the Y7 zeolite catalyst for the ring-opening reaction must be very suitable for converting aromatic hydrocarbons into lighter fractions. But proper amounts of mesopores are required for practical reactions of aromatic hydrocarbons possessing larger molecular size than the model compounds.

Another approach for developing a highly active zeolite catalyst was also carried out using commercially available Y (Y5) zeolites. In this approach, the crystallinity retention during the USY preparation was minimized, followed by effective loading of active metals onto the USY to give the HY activity. Fig. 10 shows two-stage upgrading and accelerated aging tests over the newly prepared zeolite catalyst. Light cycle oil (LCO) obtained from FCC process and the coal-derived gas oil were used for the two-stage upgrading and the accelerated aging tests, respectively. Before the HC reaction over the zeolite catalyst (second-stage upgrading), first-stage upgrading was performed for the aromatic hydrogenation and hetero-atom removal using the originally prepared HY catalyst (Cat. C in Fig. 3(a)). Lighter fractions were easily produced at lower temperature in the second-stage hydrocracking. The deactivation of the HC catalyst during the accelerated aging test was less than that of the originally prepared zeolite catalyst in Fig. 3(b). This newly prepared zeolite catalyst showed considerable improvements in the HC activity and deactivation.

If the well-crystallized NaY7 zeolites are successfully modified to well-crystallized USY zeolites possessing proper physical and chemical properties, much higher catalytic performance will be obtained for the practical HC reactions. However, the dealumination behavior of the NaY7 zeolite was different from that of the NaY5 zeolite, showing that the modification technique which was already established for the NaY5 zeolite is not available. In the course of the preparation of the well- crystallized USY zeolites, further research and development are required for optimizing the properties of the USY zeolites such as dealumination and meso-pore structures.

In conclusion, at the present stage the application of the well-crystallized USY7 zeolites to the preparation of the HC catalysts seems to be the most promising approach for developing a new HC catalyst with superior catalytic performance. But a lot of subject areas have to be worked out in order to develop the practical HC catalyst and HC process.

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