

# Catalytic Cracking of Polyethylene-Liquefied Oil over Amorphous Aluminosilicate Catalysts

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Polyethylene was thermally cracked at 425, 450, and 475 °C in nitrogen at atmospheric pressure for 10–120 min. The major components of the oil were straight-chain olefins which contained 4–25 carbons. Pyrolysis at lower temperatures for shorter reaction times produced straight-chain olefins with a broad distribution of carbon atoms, and pyrolysis at 450 °C for 60 min or under more severe conditions produced mainly straight-chain olefins containing 4–12 carbons. The reaction at 475 °C produced C<sub>1</sub>–C<sub>4</sub> hydrocarbon gases and coke by the secondary cracking and polymerization. The oil was then cracked over catalysts at 500 °C for 2 s at a heating rate of 3000 °C/s using a Curie-point pyrolyzer in a flow of helium at atmospheric pressure. Metal-loaded and dealuminated Y-zeolites as well as aluminosilicate MCM-41 were prepared and examined as cracking catalysts, and their catalytic activities and selectivities were compared to those of conventional zeolite catalysts. Aluminosilicate MCM-41 of Si/2Al = 25 and Ni–HY zeolite of Si/2Al = 50 exhibited a mild cracking activity, giving products of the middle distillate range with no coke deposition. The metal-loaded and metal-free HY zeolites of Si/2Al = 16 exhibited an excessive cracking activity, producing C<sub>5</sub>–C<sub>7</sub> olefins with coke deposition. *n*-Octadecane was used as the model compound and was cracked over the catalysts under the same conditions as those used for the polyethylene oil. The reactivity of the catalysts was well-correlated with the amount of NH<sub>3</sub> adsorption per unit catalyst area. The metal-supported dealuminated Y-zeolites and aluminosilicate MCM-41 possessed less aluminum atoms and, as a result, a smaller number of acidic sites. The removal of aluminum atoms from the zeolite framework and the control of the acidity are thus key factors in achieving mild cracking of the paraffinic oil.

## Introduction

Liquefaction of plastic wastes is an important technology to utilize these materials as carbon resources,<sup>1–3</sup> and many studies have been reported on cracking of plastics and upgrading of plastic-derived oils with and without catalysts and on reaction mechanisms.<sup>4–13</sup> Waste plastics, which are produced in urban areas, are composed of polyethylene (PE), polystyrene (PS), polypropylene (PP), poly(vinyl chloride) (PVC), and polyethyleneterephthalate (PET), the sum of which is ap-

proximately 70% of the total plastics wastes.<sup>1</sup> However, PVC and acrylonitrile–butadiene–styrene copolymer (ABS) contain chlorine and nitrogen, respectively, and give rise to HCl and HCN during cracking reactions. PET contains oxygen, and these plastics are usually removed by gravity separation prior to cracking. Waste plastics are then thermally cracked at 300–500 °C under atmospheric pressure. The liquid products are upgraded to transportation fuel using zeolites or metal catalysts.

In earlier papers,<sup>14,15</sup> we have reported that the product selectivity for the hydrocracking of vacuum gas oil from an Arabian crude is controlled by dealuminating and metal-loading of the Y-zeolite catalysts. Optimally designed catalysts produce gasoline and gas oil in large yields and gas and coke in small yields. The balance between hydrogenation and cracking activity, originating from the supported metals and Brønsted acid sites, is critically important for the selective hydrocracking. Rapid heating of reactants and a short contact time, as in fluid catalytic cracking process (FCC), are expected to contribute to a large yield of middle distillate. Under these conditions, secondary cracking of products are effectively suppressed.

- (1) Kaji, M. *J. Jpn. Energy Inst.* **1996**, 75, 778.
- (2) Nishio, S.; Ueno, A.; Ohkita, H.; Kakuta, N. *J. Jpn. Catal. Soc.* **1994**, 36, 342.
- (3) Williams, V. *Symp. Waste Plastic Recycl., Jpn. Polym. Soc.* **1993**, Tokyo.
- (4) Murata, K.; Makino, T. *Nippon Kagaku Kaishi* **1973**, 2414.
- (5) Tsuchiya, Y.; Sumi, K. *J. Polym. Sci.* **1968**, 6, 415.
- (6) Murata, K.; Makino, T. *Nippon Kagaku Kaishi* **1975**, 192.
- (7) Uemichi, Y.; Kashiwaya, Y.; Ayame, A.; Kanoh, H. *Chem. Lett.* **1984**, 41.
- (8) Audisio, G.; Silvani, P.; Beltrame, P.; Carniti, P. *J. Anal. Appl. Pyrolysis* **1984**, 7, 83.
- (9) Beltrame, P.; Carniti, P.; Audisio, G.; Bertini, P. *Polym. Degrad. Stab.* **1989**, 26, 209.
- (10) Ohkita, H.; Nishiyama, R.; Tochiara, Y.; Mizushima, T.; Kakuta, N.; Morioka, Y.; Ueno, A.; Namiki, Y.; Tanifuji, S.; Katoh, H.; Sunazuka, H.; Nakayama, T.; Kuroyanagi, T. *Ind. Eng. Chem. Res.* **1993**, 32, 3112.
- (11) Miyake, A.; Kimura, K. *Polym. Dig.* **1993**, 1, 6.
- (12) Saito, K. *Symp. Res. Resources* **1990**, 37.
- (13) Hirota, K. *Symp. Waste Plastic Recycl., Jpn. Polym. Soc.* **1993**, 9.

- (14) Isoda, T.; Kusakabe, K.; Morooka, S. *Proc.-Am. Chem. Soc., Div. Pet. Chem.* **1997**, 42, 420.
- (15) Isoda, T.; Kusakabe, K.; Morooka, S.; Mochida, I. *Energy Fuels* **1998**, 12, 493.

Table 1. Properties of Catalysts

catalyst	metal content (wt %)	Si/2Al	surface area (m <sup>2</sup> /g)	amount of adsorbed NH <sub>3</sub> (mmol/g)
HY-A	0	16.1	794	0.83
Ni-HY-A-1	6.5 <sup>a</sup>	16.0	693	0.61
Ni-HY-A-2	9.2 <sup>a</sup>	16.0	693	0.57
Ni-HY-B	11.5 <sup>a</sup>	50.0	568	0.50
Co-HY	9.9 <sup>b</sup>	16.0	708	0.61
Fe-HY	8.9 <sup>c</sup>	18.0	710	0.68
H-ZSM5	0	50.0	350	0.56
aluminosilicate	0	25.0	850	0.54
MCM-41				
i.d.	0	50.0	892	0.40
i.d.	0	100.0	736	0.28
i.d.	0	200.0	1007	0.18

<sup>a</sup> NiO. <sup>b</sup> CoO. <sup>c</sup> Fe<sub>2</sub>O<sub>3</sub>.

In the present study, Ni-, Co-, and Fe-supported dealuminated Y-zeolites and aluminosilicate MCM-41, an amorphous silicate, are prepared. Heavy oil produced by the thermal cracking of polyethylene at 425–475 °C is mixed with each catalyst and is cracked in a Curie-point pyrolyzer at 500 °C for 2 s in a flow of helium at atmospheric pressure. This simulates the feasibility of a short contact time process such as FCC for upgrading the heavy oil. Deactivation of the catalysts, which is an important factor for utilizing acidic zeolites, is neglected in the present study.

## Experimental Section

**Preparation of Catalysts.** (1) Ni-, Co-, and Fe-loaded Y-zeolites were prepared according to the literature:<sup>14–16</sup> Na-Y zeolite (Na<sub>2</sub>O content = 13.3 wt %, Si/2Al = 5.0) was ion-exchanged with NH<sub>4</sub><sup>+</sup> and was then calcined (hereafter referred to as HY). It was further treated with steam at 670 °C to dealuminate the zeolite to different degrees and then obtained USY zeolite (hereafter referred to as HY-A and HY-B). The compositions of HY-A and HY-B were Si/2Al = 16.0 and 50.0, respectively, and Na<sub>2</sub>O = 1.2 wt % for both catalysts. A 500-g portion of each HY zeolite was suspended in 5 L water at 75 °C, and 3 L of a 12 N HNO<sub>3</sub> and Ni(NO<sub>3</sub>)<sub>2</sub> solution (0.5 mol/L of Ni, pH = 1.1) was then added to the slurry with stirring. After the mixture was stirred for 0.5 h at 75 °C, 3 L of a 12 N HNO<sub>3</sub> and Ni(NO<sub>3</sub>)<sub>2</sub> solution (1.0 mol/L of Ni) was added with continued stirring. A 5% aqueous ammonia solution was also added to maintain the pH at 4.0. After the mixture was stirred for 0.5 h, the catalyst was filtered, washed, and dried at 120 °C for 4 h. The impregnation of other metals was performed by a similar method. The properties of the metal-supported Y-zeolites are summarized in Table 1.

(2) An aluminosilicate MCM-41 catalyst was prepared as follows:<sup>17,18</sup> Sodium aluminate (NaAlO<sub>2</sub>, Wako Chemical Ind.) and tetraethoxysilane (TEOS, Wako Chemical Ind.) were used as the aluminum and silica sources for the zeolite synthesis. Tetramethylammonium hydroxide (TMAOH, Wako Chemical Ind.) and hexadecyltrimethylammonium chloride (C<sub>16</sub>TMACl, Aldrich) were used as the template reagents. C<sub>16</sub>TMACl was dissolved in an aqueous TMAOH solution at 50 °C with stirring, and NaAlO<sub>2</sub> was then added to the solution at room temperature. TEOS was added dropwise to the stirred solution. The molar ratio of templates and water to SiO<sub>2</sub> was fixed

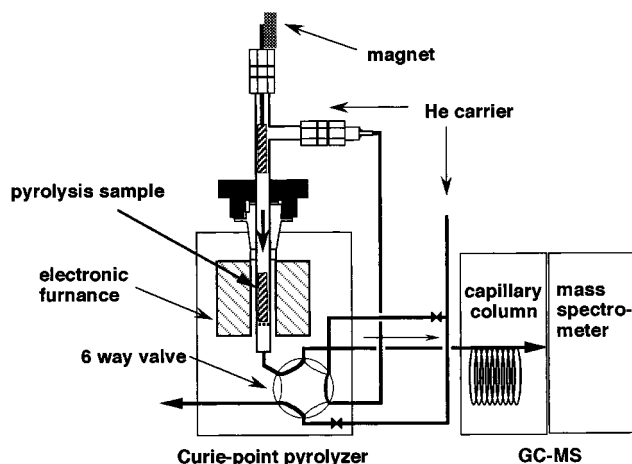


Figure 1. A schematic view of Curie-point pyrolyzer equipped with a GC-MS system.

at SiO<sub>2</sub>:(C<sub>16</sub>TMA)<sub>2</sub>O:(TMA)<sub>2</sub>O:H<sub>2</sub>O = 1:0.2:0.5:110. The molar ratio of NaAlO<sub>2</sub> to SiO<sub>2</sub> was varied over a range of 0.01–0.2.

Hydrothermal synthesis was performed using a batch autoclave at 110 °C for 24 h without stirring. The solid particles were separated, washed with water several times, and dried at room temperature under vacuum. The solid was calcined in air at 550 °C for 2 h to remove the templates in the lattice of the zeolite crystal. The catalyst was further ion-exchanged to the proton form in an aqueous NH<sub>4</sub>OH solution (1 mol/L) at 50 °C for 6 h and calcined at 500 °C for 2 h in a flow of air prior to use. The catalysts were characterized by XRD (Cu Kα radiation), BET, and NH<sub>3</sub>-TPD. The properties of the zeolites are summarized in Table 1.

**Thermal Cracking of Polyethylene.** Polyethylene (PE; Mitsui Petrochemical Ind.) was selected because the composition of its thermally cracked oil was very similar to that of vacuum gas oil from an Arabian crude,<sup>15</sup> a typical feedstock of the FCC process. Thermal cracking of PE was performed using 5 g of the substrate in a 30-mL high-pressure tube bomb. The reactor was then filled with nitrogen at 0.5 MPa and placed in a salt bath at 425, 450, and 475 °C. After a reaction for 10–120 min, the reactor was placed in water. The weight loss due to the release of the gas was ascribed to the formation of C<sub>1</sub>–C<sub>3</sub> hydrocarbons.

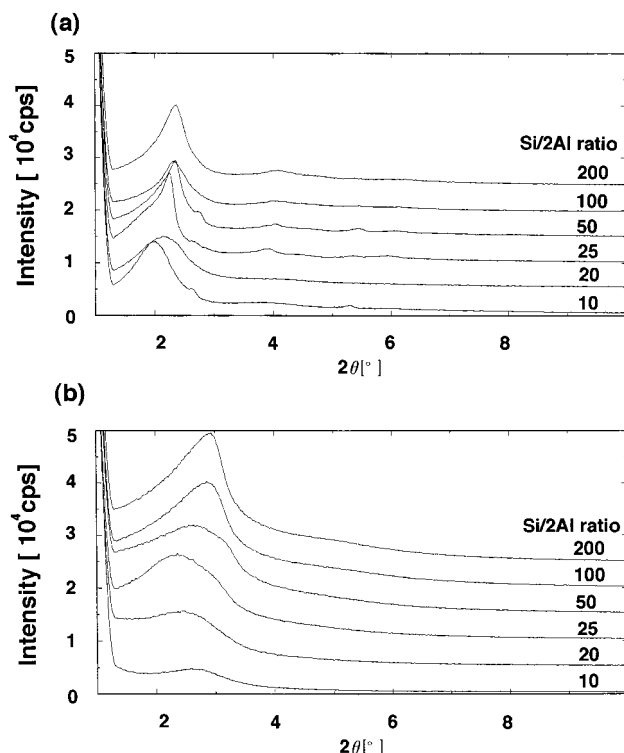
The liquid product was recovered by benzene and fractionated with benzene into a benzene-soluble (BS) fraction and a benzene-insoluble (BI) fraction. The former is hereafter referred to as PE oil. The latter fraction contained unreacted polyethylene. Carbonaceous materials, which were deposited on the reactor wall, were recovered and defined as coke. After removal of the solvent, BS, BI, and coke were dried under vacuum at 90 °C for 6 h and weighed and the yields of each were calculated. The yield of each hydrocarbon component, carrying a straight-chain with a small number of unsaturated bonds, in the BS fraction was determined by qualitative and quantitative analyses using a GC-MS (QP-5000, Shimadzu) and a GC-FID (GC-14A, Shimadzu), equipped with a capillary column.

**Catalytic Cracking Reaction.** Figure 1 shows the equipment used for catalytic cracking. The PE oil, as well as *n*-octadecane used as the model compound, was cracked using a Curie-point pyrolyzer (Japan Analytical Industry, JHP-2) in a flow of helium under atmospheric pressure. A mixture of catalyst and substrate, containing 10 wt % of substrate on 2-mg of catalyst, was tightly wrapped in a ferromagnetic foil, the Curie-point temperature of which was 500 °C. The heating rate was approximately 3000 °C/s, and the total pyrolysis time was fixed at 2.0 s. The temperature of the reactor zone was kept at 250 °C. All volatiles were rapidly transported from the reaction zone by the helium gas flow to minimize any

(16) Jpn. Patent 09-59649, 1977.

(17) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Lenowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(18) Karen, J.; White, J. H. *J. Chem. Soc., Chem. Commun.* **1995**, 155.

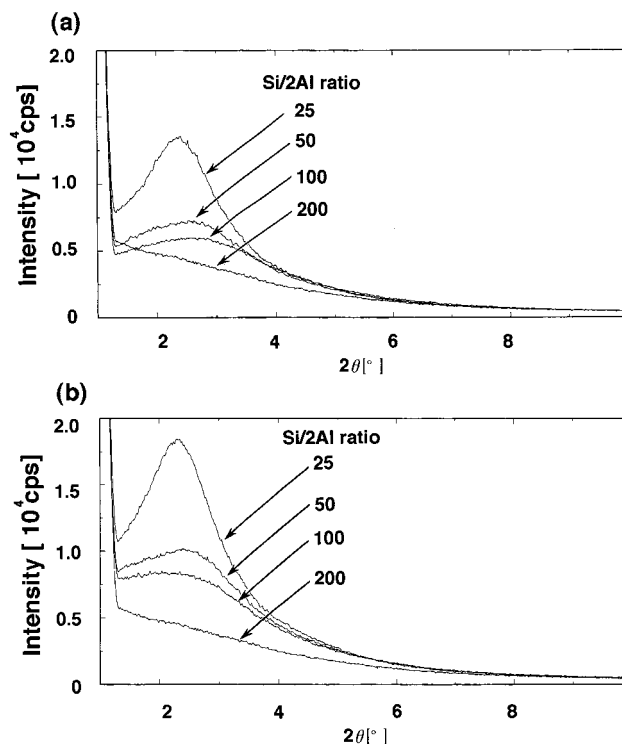


**Figure 2.** XRD profiles of aluminosilicates MCM-41 (a) after hydrothermal synthesis and (b) after calcination.

secondary cracking reactions in the gas phase. No liquid products were found after the cracking reaction. Yields of hydrocarbons were qualitatively and quantitatively analyzed using the GC-MS equipped with a capillary column, which was directly connected to the pyrolyzer. The catalytic cracking reaction was carried out at least in triplicate under the same conditions to ensure data reliability. Coke deposition was determined by elemental analysis of the used catalyst.

## Results

**Effects of Calcination and  $\text{NH}_4^+$  Exchange on the Structure of Aluminosilicate MCM-41.** Figure 2 shows XRD profiles of aluminosilicates MCM-41 with different Si/2Al ratios (a) after hydrothermal synthesis and (b) after calcination successive to the synthesis. A large, broad peak was observed at  $2-2.5^\circ$  and was assigned to (100) of MCM-41.<sup>17,18</sup> The aluminosilicates MCM-41 were amorphous with some structure under the conditions examined in the present study. The peak, which was observable for all aluminosilicates MCM-41 without calcination as shown in Figure 2a, was decreased as a result of calcination. As shown in Figure 2b, the structures of the aluminosilicates MCM-41, which had Si/2Al ratios less than 20, were completely collapsed by the calcination. Figure 3 shows the effect of ion exchange on XRD profiles for the protonated aluminosilicates MCM-41. The XRD peak at  $2.0-2.5^\circ$  for the aluminosilicates MCM-41 having Si/2Al ratios larger than 50 disappeared as a result of contact with water. However, aluminosilicate MCM-41 having Si/2Al = 25 was stable during the  $\text{NH}_4^+$  exchange and calcination at  $500^\circ\text{C}$ , as indicated in Figure 3b. The acid strength of the protonated aluminosilicate MCM-41, as determined by  $\text{NH}_3$ -TPD, is summarized in Table 1. The amount of  $\text{NH}_3$  desorption increased with a decrease in the Si/2Al ratio. The acid strength of the



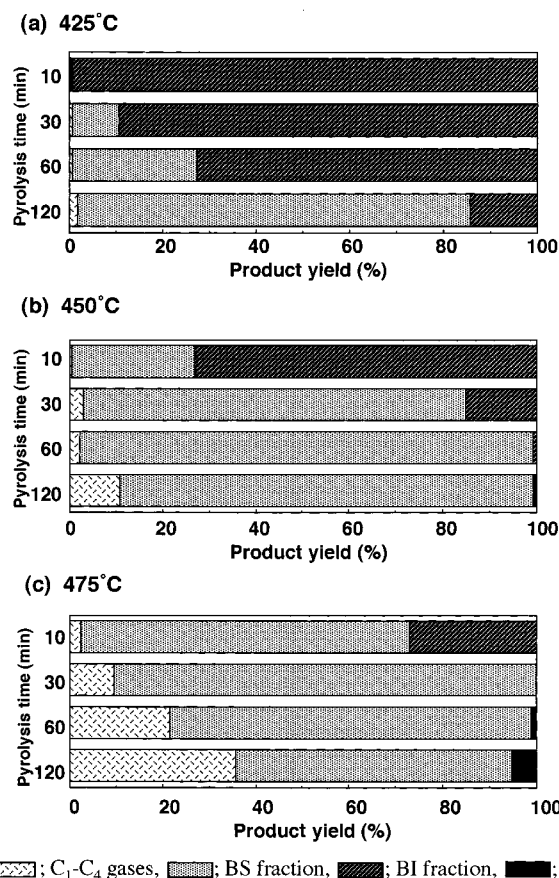
**Figure 3.** XRD profiles of protonated aluminosilicates MCM-41 ion-exchanged in ammonium solution for (a) 0 min and (b) 6 h.

aluminosilicate MCM-41 is related to the Si/2Al ratio since Brönsted-acid sites originate from Al—OH bonds.<sup>19</sup>

**Product Distributions from Thermal Cracking of PE.** Figure 4 shows product yields based on the initial mass of PE, from thermal cracking at  $425-475^\circ\text{C}$  under a nitrogen atmosphere of 0.5 MPa. The thermal cracking produced a heavy oil, which was waxy at room temperature. At a reaction temperature of  $425^\circ\text{C}$ , the BS fraction was 10% after cracking for 30 min, 25% for 60 min, and 85% for 120 min. The cracking reaction was significantly enhanced by an increase in the reaction temperature, and the PE was completely cracked by reaction for 60 min at  $450^\circ\text{C}$ . No coke was formed at temperatures of  $425$  and  $450^\circ\text{C}$ . Hydrocarbon gases, representing  $\text{C}_1-\text{C}_4$  compounds, were produced at a yield of 10% by cracking at  $450^\circ\text{C}$  for 120 min. The yield of gaseous products increased to 10–35% for the case of cracking at  $475^\circ\text{C}$  for 30–120 min. The coke yield reached 7% for cracking at  $475^\circ\text{C}$  for 120 min. Murata et al.<sup>4</sup> reported that PE was cracked at temperatures above  $290^\circ\text{C}$ , producing a waxy oil and no gaseous hydrocarbons, and that cracking reactivity increased with increasing temperature above  $370^\circ\text{C}$ . Our results are in agreement with their conclusions.

Figures 5–7 show product distributions in BS fractions produced under different cracking conditions. The major components of the BS fraction produced at  $425^\circ\text{C}$  were straight-chain olefins containing 5–30 carbons for all reaction times employed. The yield of each carbon number group was 0.5–5%. Similar trends were found for BS fractions formed by cracking at  $450^\circ\text{C}$  for 10 and 30 min. Major components were shifted to *n*-olefins of  $\text{C}_5-\text{C}_{10}$  for the BS fraction formed at  $450^\circ\text{C}$  for 30 min. The yield of each carbon number group



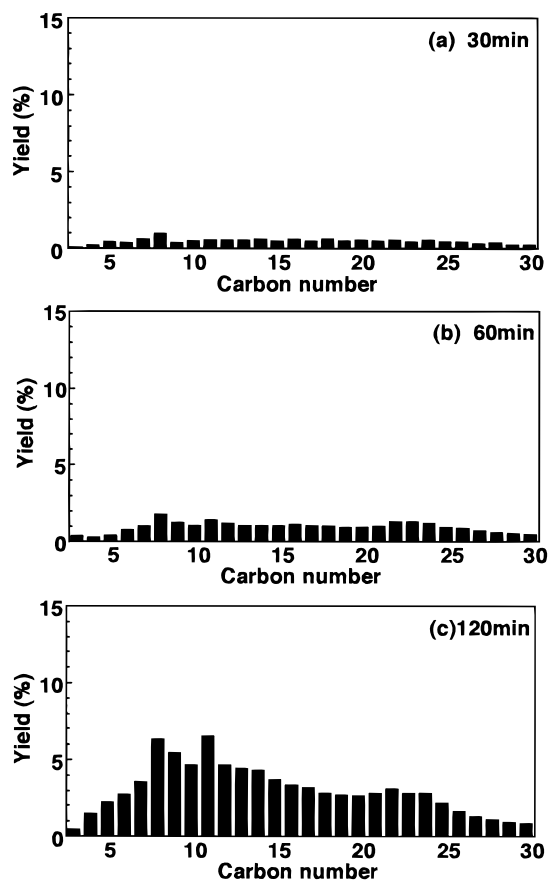


**Figure 4.** Components of thermal cracking products from polyethylene.

was 7–12%, and *n*-olefins of C<sub>11</sub>–C<sub>25</sub> were also produced in yields of 2–5%. When the reaction time was extended to 120 min, the major components were shifted to *n*-olefins of C<sub>4</sub>–C<sub>10</sub> and the yield of each carbon number group was 5–10%. The overall trend was the same for the cracking at 475 °C. However, secondary cracking and polymerization of the product oil proceeded and C<sub>1</sub>–C<sub>4</sub> gases as well as coke were formed.

**Product Distribution from Catalytic Cracking of *n*-Octadecane.** Figure 8 shows product distributions for the catalytic cracking of *n*-octadecane, used as the model compound, over the aluminosilicates and zeolites at 500 °C for 2 s under atmospheric pressure in a flow of helium. *n*-Octadecane was not cracked without the catalysts under the present conditions as well as the short reaction time. *n*-Pentene and *n*-hexene were found in the product for all catalysts examined. The ZSM-5 exhibited the highest activity for the cracking of *n*-octadecane and gave a conversion of 80%. The catalyst activity of metal-loaded HY zeolites decreased with increasing amount of metal, and the conversion was 65% over the Ni–HY–A (metal loading = 10 wt %) and Fe–HY catalysts (metal loading = 6.5 wt %), 60% over the Ni– and Co–HY catalysts (metal loading = 10 wt %), and 75% over the metal-free HY zeolite. The conversion was greatly decreased to 15% when the dealuminated Ni–HY–B zeolite of Si/2Al = 50 was used. The aluminosilicates MCM-41 of Si/2Al = 25 and 200 showed conversions of 20% and 10%, respectively.

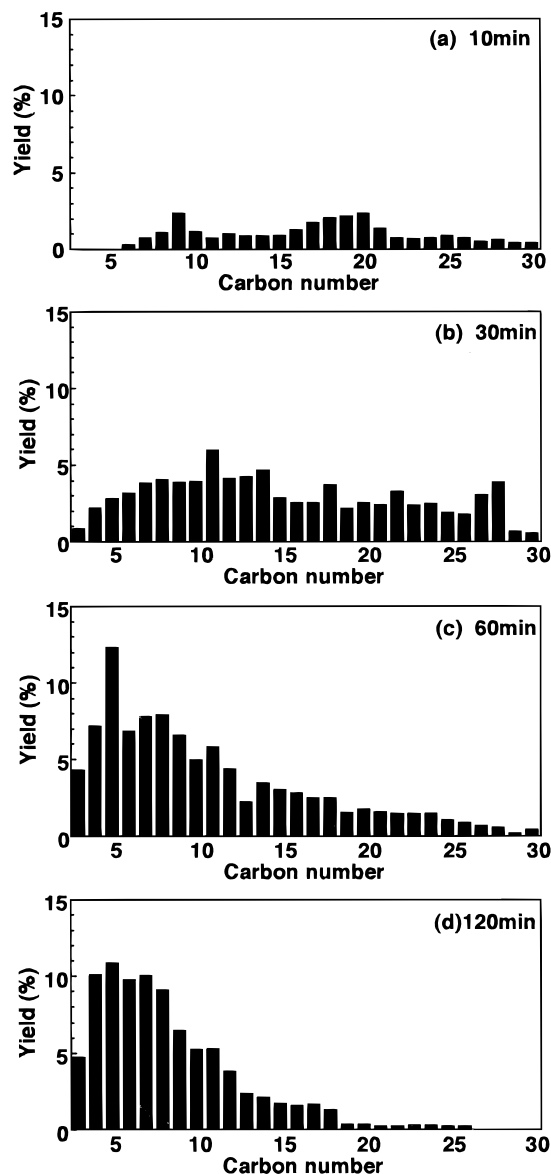
Figure 9 illustrates the product distribution for the catalytic cracking of PE oil produced at 450 °C. The catalytic reactions were carried out under the same



**Figure 5.** Distributions of *n*-paraffins in the benzene-soluble fraction from PE oil. Reaction temperature, 425 °C.

conditions as those described above. The catalysts tested were thus classified into two categories: (1) catalysts with high cracking activity, producing hydrocarbons containing less than six carbons (the ZSM-5 and Co- and Fe-supported dealuminated Y-zeolites were included in this group) and (2) catalysts which selectively produced a middle distillate without coke deposition and minimized the production of light olefins. The Ni-supported dealuminated Y-zeolites and aluminosilicate MCM-41 were included in this group. The catalytic activity of these catalysts increased with increasing amount of NH<sub>3</sub> adsorption, as shown in Table 1. This suggests that the catalytic cracking activity is related to the amount of acid sites for a single-component substrate such as *n*-octadecane.

**Product Selectivity from the Catalytic Cracking of PE Oil.** Figures 10–12 show the product yields for the catalytic cracking of PE oils produced by thermal cracking at 450 °C for 0.5, 1, and 2 h as a function of the amount of NH<sub>3</sub> adsorption per unit surface area of catalyst. The catalytic reaction conditions were the same as those used for *n*-octadecane. A good correlation between the product yield and the amount of NH<sub>3</sub> adsorption per unit surface area was found for the catalysts examined, whereas the yield was not related to the acidity per unit catalyst mass. The latter is usable to compare catalysts possessing similar surface areas. The catalysts used in this study, however, have a wide variety of surface areas per unit mass. For instance, the surface area per unit mass of aluminosilicate MCM-41 is 2.5 times larger than that of ZSM-5.

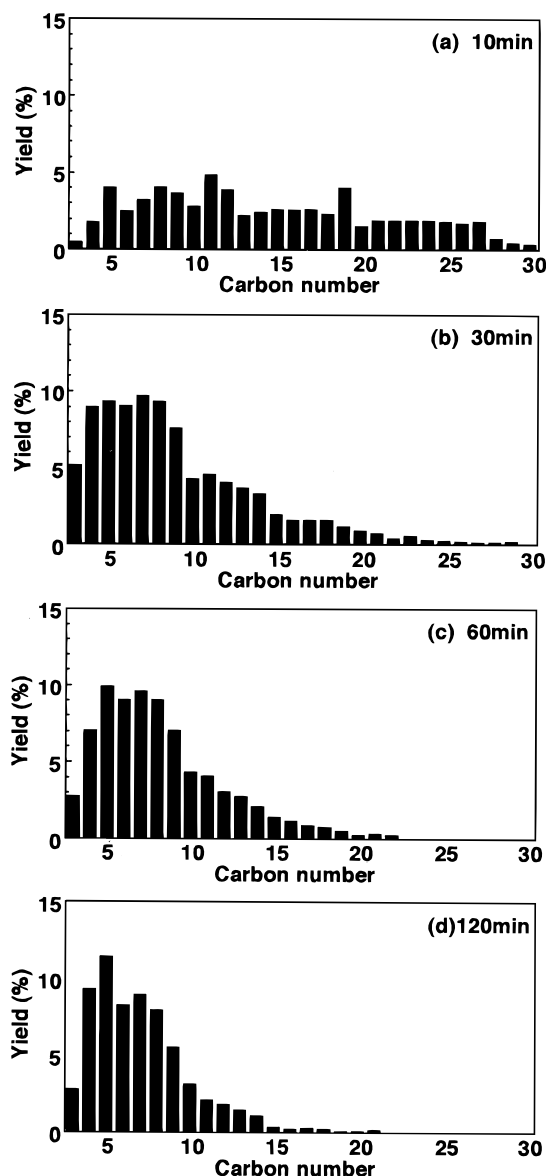


**Figure 6.** Distributions of *n*-paraffins in the benzene-soluble fraction from PE oil. Reaction temperature, 450 °C.

The correlation based on the catalyst surface area is thus justifiable.

As indicated in Figures 10a–12a, the ZSM-5, HY-A, and Fe-HY zeolites produced C<sub>1</sub>–C<sub>6</sub> fractions at yields of 50–55 wt % for all PE oils. The yield was 50 wt % over Ni-HY-A-2 loaded with 6.5 wt % NiO, 40 wt % over Ni-HY-A-1 loaded with 9.5 wt % NiO, 30–35 wt % over the aluminosilicate MCM-41s, and 28 wt % over the Ni-HY-B. Thus, the yields of C<sub>1</sub>–C<sub>6</sub> fractions were decreased with decreasing acid sites per unit surface area of catalyst.

On the other hand, the yields of C<sub>11</sub>–C<sub>14</sub> and C<sub>15</sub>–C<sub>18</sub> fractions increased with decreasing acid sites per unit surface area of catalyst as shown in Figures 10b–12b and Figures 10c–12c, respectively. The yields of the middle distillate were increased for the PE oil derived by the thermal cracking for 1 and 2 h, when the aluminosilicate MCM-41s or Ni-HY-B of Si/2Al = 50 were used. The aluminosilicate MCM-41s of Si/2Al = 100 and 200 gave middle distillate yields of 17–23 and 20–25 wt %, respectively. In contrast, the Ni-HY, Co-HY, and Fe-HY of Si/2Al = 16 and ZSM-5 catalysts



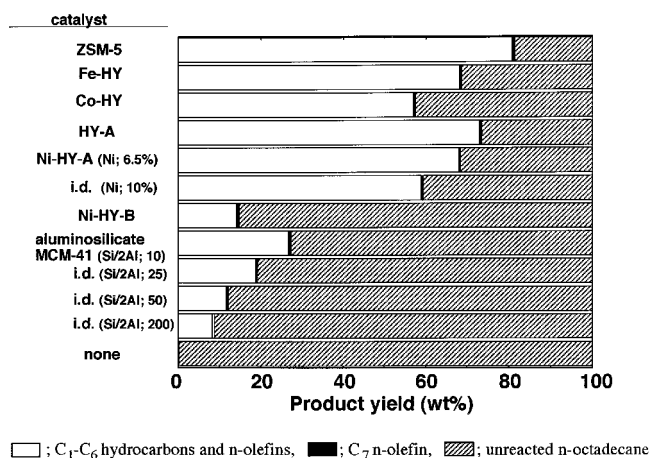
**Figure 7.** Distributions of *n*-paraffins in the benzene-soluble fraction from PE oil. Reaction temperature, 475 °C.

which carried high acidity gave lower yields than the aluminosilicate MCM-41s and Ni-HY-B.

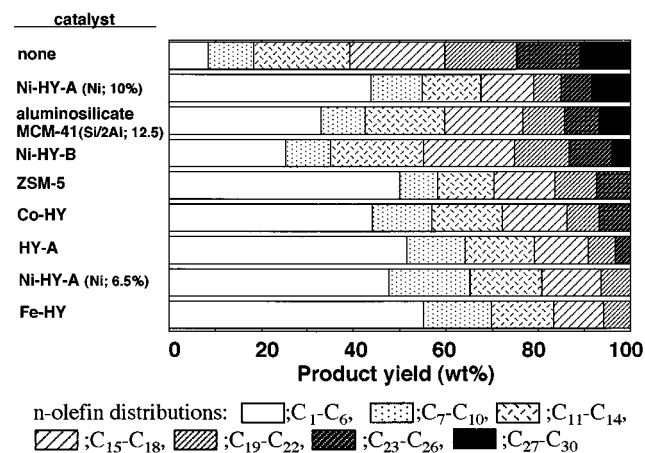
## Discussion

**Acidity Control for Amorphous Silicate Catalysts.** Crystalline microporous molecular sieves, such as Y-zeolites, mordenite, ZSM-5, and AlPO<sub>4</sub>, contain channels and cavities of 0.5–1.5 nm and are widely used as commercial catalysts and sorbents, especially in petrochemical processes. There has been an increasing demand for molecular sieves with a pore diameter in the mesopore range for the treatment of heavier feeds and the production of higher molecular weight chemicals. Most of the synthetic zeolites have in a limited range of Si/2Al ratios and possess a strong acidity. This often leads to excessive cracking of heavy oil, producing the light hydrocarbons.

Dealumination of the parent zeolites is effective in reducing acidity. Aluminum atoms in the structure are substituted by silica atoms, originating from the partially decomposed portion of the zeolite, as reported



**Figure 8.** Product distributions by catalytic cracking of *n*-octadecane.



**Figure 9.** Product distributions by catalytic cracking of PE oil derived at 450 °C for 1 h.

previously.<sup>20</sup> This dealumination treatment also provides mesopores in the zeolite structure. These structural changes have been confirmed by TEM observation.<sup>21</sup> In the present study, the change in acidity was evaluated based on catalytic cracking reactivity, as well as  $\text{NH}_3$  desorption and pore size distribution. The combination of dealumination and supported metal effectively decreases the acidity of the parent HY zeolite. We reported earlier that a metal-free HY zeolite exhibited higher hydrocracking activity for vacuum gas oil than that of a Ni-supported HY zeolite.<sup>14,15</sup> The Ni-HY catalyst, which possessed the optimized acidity, produced a large amount of middle distillate, while the metal-free HY zeolite mainly produced gaseous products such as  $\text{C}_1$ – $\text{C}_4$  olefins.

In contrast, molecular sieve MCM-41, which contained uniform one-dimensional channels 1.6–10 nm in diameter, was recently synthesized at Mobil.<sup>17</sup> However, this material is unsuitable as a catalyst for the cracking. The crystal structure of aluminosilicate MCM-41 is unstable during the proton-exchange step in aqueous solution and is a problem from the industrial utilization point of view. Aluminum atoms in the structure of aluminosilicate MCM-41 are displaced by a mild thermochemical treatment as reported previ-

ously.<sup>22</sup> Nanba et al.<sup>23</sup> reported that the structure of MCM-41 was readily deteriorated on exposure to hot water and that the FMS-16 structure, a mesoporous material synthesized from Kanemite ( $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ ), was stable. As shown in Figures 2 and 3, however, the aluminosilicate MCM-41 of  $\text{Si}/2\text{Al} = 25$  maintains its structure during the calcination and ion-exchange steps while aluminosilicates having other  $\text{Si}/2\text{Al}$  ratios are easily collapsed.

Chen et al.<sup>24</sup> found that FSM-16 was superior to the MCM-41 zeolite with respect to thermal stability because the polymerization degree of the silicate structure in FMS-16 was higher than that in MCM-41, although the physical properties of both materials were very similar. MCM-41 prepared by Edler and White<sup>25</sup> achieved a higher degree of polymerization of the silicate structure by aging for 3 days and was stable during drying, washing, and calcination treatments. These results suggest that the stability of MCM-41 is determined by the degree of polymerization of the silicate structure, which, in turn, can be controlled by  $\text{Si}/2\text{Al}$  ratio.

**Difference in Catalysis of PE Oil and Model Compound.** The PE oil has been characterized as (1) being primarily straight 1-olefins, (2) having practically no branched olefins and aromatics, and (3) having a wide product distribution.<sup>26</sup> Thermal cracking of PE is initiated by elimination of a proton at the end of the substrate, and 1-olefins and propylene are produced by a radical mechanism.<sup>5</sup> Thus, product selectivity is difficult to control by thermal decomposition, and catalytic cracking of the PE oil is required in order to increase the yield of middle distillate. Upgrading using acid catalysts such as silica–alumina or protonated ZSM-5 zeolite produces aromatics and branched hydrocarbons.<sup>7</sup> In contrast, no aromatics are found in products over the catalysts which possess a small amount of acid sites, as examined in the present study.

The catalyst activity which is evaluated by the cracking of *n*-octadecane using a flash pyrolyzer is directly related to the  $\text{NH}_3$  desorption. However, the cracking reactivity of *n*-octadecane is greatly different from that of PE oil. Mono-olefins are effectively cracked over catalysts such as HY, Ni-HY, Co-HY, Fe-HY, and ZSM-5 zeolites, which have abundant acid sites on the surface. The cracking reactivity of long alkyl chains is higher than that of short alkyl chains. When they are fed as a mixture, the cracking reaction of short alkyl chain olefins is hindered by competitive reactions of long-chain olefins, which are selectively adsorbed on a limited number of acidic sites on catalysts such as aluminosilicate MCM-41 and Ni-HY-B zeolite of a high  $\text{Si}/2\text{Al}$  ratio. Thus, the acidity, as well as the number of acid sites, is a fundamental factor which describes the catalyst activity.

(22) Luan, Z.; He, H.; Zhou, W.; Chen, C.-F.; Kinowski, J. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 2955.

(23) Nanba, S. *44th Meeting Jpn. Pet. Inst.* **1995**, 178.

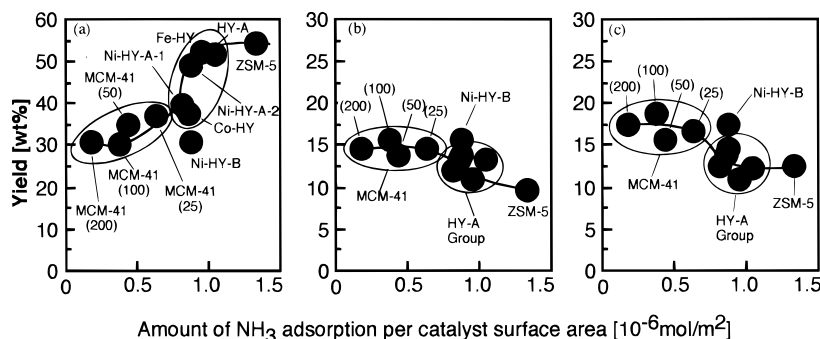
(24) Chen, C. Y.; Xiao, S. Q.; Davis, M. E. *Microporous Mater.* **1995**, 4, 1.

(25) Edler, K. J.; White, J. W. *J. Chem. Soc., Chem. Commun.* **1995**, 155.

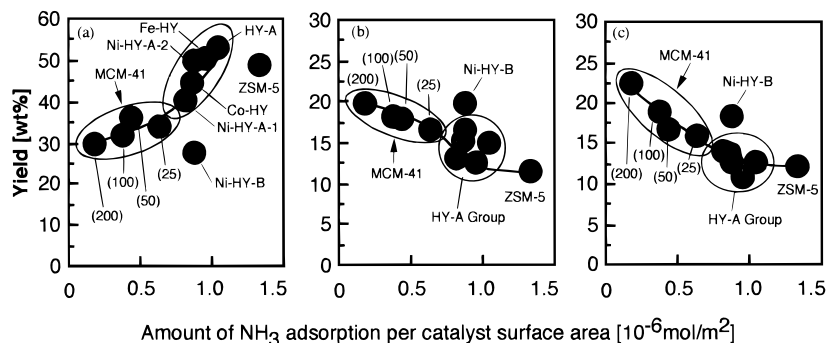
(26) Nishizaki, H.; Sakakibara, M.; Yoshida, K.; Endo, K. *Nippon Kagaku Kaishi* **1977**, 1879.

(20) Kerr, G. T. *Molecular Sieves*; ACS monograph; American Chemical Society: Washington, DC, 1974; Vol. 121, p 219.

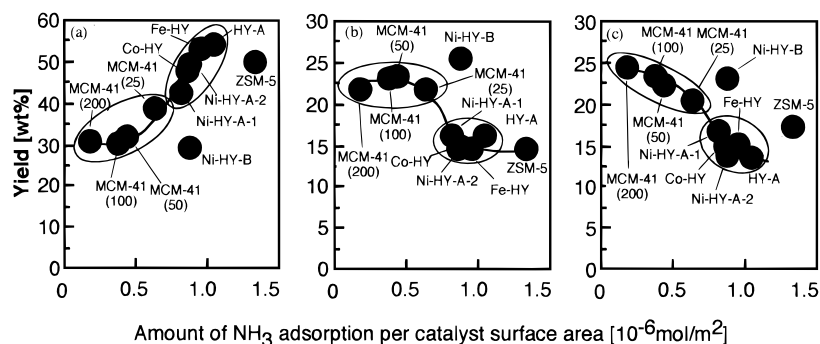
(21) Lohse, U. Z. *Anorg. Allg. Chem.* **1980**, 460, 179.



**Figure 10.** Product distributions by catalytic cracking of PE oil derived at 450 °C for 0.5 h. (a)  $\text{C}_1\text{--C}_6$ , (b)  $\text{C}_{11}\text{--C}_{14}$ , and (c)  $\text{C}_{15}\text{--C}_{18}$  paraffins.



**Figure 11.** Product distributions by catalytic cracking of PE oil derived at 450 °C for 1 h. (a)  $\text{C}_1\text{--C}_6$ , (b)  $\text{C}_{11}\text{--C}_{14}$ , and (c)  $\text{C}_{15}\text{--C}_{18}$  paraffins.



**Figure 12.** Product distributions by catalytic cracking of PE oil derived at 450 °C for 2 h. (a)  $\text{C}_1\text{--C}_6$ , (b)  $\text{C}_{11}\text{--C}_{14}$ , and (c)  $\text{C}_{15}\text{--C}_{18}$  paraffins.

## Conclusions

(1) Aluminosilicate MCM-41 of  $\text{Si}/2\text{Al} = 25$  maintained its structure during calcination in air and  $\text{NH}_4^+$ -exchange treatment. This catalyst provided the optimum acidity for the cracking reaction of PE oil. Aluminosilicates MCM-41 of higher  $\text{Si}/2\text{Al}$  ratios were collapsed on contact with water.

(2) A combination of dealumination and supported metals effectively decreased the acidity of HY zeolite.

(3) Catalytic activity, which was evaluated from the cracking of *n*-octadecane, was related to the amount of acid sites determined by  $\text{NH}_3$  desorption. However, the

catalytic cracking reactivity of PE oil was different from that of *n*-octadecane. Long alkyl-chain olefins in the PE oil were cracked over catalysts which possessed a small number of acid sites, retarding adsorption of short alkyl chain olefins. Thus, the cracking of longer alkyl-chain olefins proceeded selectively over the metal-supported dealuminated Y-zeolites and aluminosilicate MCM-41 catalysts, containing a limited number of acid sites. The catalyst acidity should be controlled by the composition and reactivity of each component in the feed oil.

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