Liquid-phase degradation of polyethylene wax over mordenite catalysts with different Si/Al molar ratios

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The catalytic liquid-phase degradation of polyethylene wax into fuel oil was studied using mordenite catalysts with various Si/Al molar ratios prepared by dealumination. The total yield of gas and liquid products showed a volcano plot along the Si/Al molar ratio of mordenite. No significant change was observed in the composition of the liquid product for all catalysts used in this study. Fast deactivation was anticipated on the mordenite catalysts with low Si/Al molar ratios such as 5 and 10, due to pore blocking by the carbon deposited on the external surface of the zeolite. A high activity and a long catalyst life were obtained on the mordenite catalyst with a Si/Al molar ratio of 12.

Keywords: polyethylene wax, mordenite, liquid-phase degradation, dealumination

1. Introduction

The effective treatment of waste polymeric materials becomes a difficult social problem due to the rapid increase in the amount of polymer production. Since the burying and incineration of polymers bring about the contamination of soil and air, various reuse methods are developed to minimize waste polymer [1–9]. On the other hand, recycling is limited to a few specific materials, so the degradation of waste polymer into a mixture of lower hydrocarbons, which can be used as a fuel, is considered to be an environmentally-friendly recycling method in respect to economy and treatment on a large scale [10,11].

Polymers are thermally degraded at high temperatures. Although the thermal degradation is very simple in terms of the principle and operation, the high energy cost and the large amounts of gas products reduce the recycling efficiency of polymer wastes [8]. A catalyst can lower the reaction temperature and increase the liquid fraction of products, thus saving energy and improving the quality of the product [12–20].

Among various acidic and basic catalysts, ZSM-5 (MFI) zeolite is used in the proposed liquefaction process, such as the Fuji catalytic degradation, due to a small amount of carbon deposition, sustaining a substantial catalyst life [14]. The particular pore structure of MFI zeolite suggests reduction in carbon deposition [21,22]. In comparison with MFI zeolite, mordenite (MOR) with a straight pore composed of 12-oxygen rings shows poor activity, because of severe pore blocking by carbon deposition [23]. But the simple and straight pore structures eliminate the pore effect on catalytic activity. Therefore, MOR catalysts with different Si/Al molar ratios may be suitable to examine the effect of the acid site concentration on catalytic degradation. Furthermore, the high structure stability of MOR zeolite enables us to prepare several MOR catalysts with different Si/Al molar ratios by dealumination with hydrochloric acid, without the collapse of the pore structure [23].

The catalytic degradation of a polymer is usually carried out at the gas phase [10,11]. The liquid-phase degradation has the advantage of being operated at a low temperature and producing high yields of liquid products. But a large amount of carbon deposition on the catalyst is a severe problem because of the close contact between catalyst particles and liquid-phase hydrocarbon molecules [12,13].

Physico-chemical properties of polymeric materials are extensively variant along their components, molecular weights, and polymerization methods. The degradation behavior is also strongly dependent on the type of polymeric materials. Polyethylene wax (PE wax), a by-product of the polyethylene polymerization process, has a low molecular weight and a linear hydrocarbon chain. The melting point of PE wax is relatively low, thus, liquid-phase degradation of PE wax is possible under moderate temperature conditions. Furthermore, the simple structure of PE wax eliminates the effect of polymer structure on catalytic degradation.

In this paper, the effects of acid site concentrations on the products yield and the products composition of the liquid-phase degradation of PE wax on MOR catalysts were studied. The MOR catalysts with various Si/Al molar ratios were prepared by dealumination treatment with hydrochloric acid solutions. The optimum concentration of the acid sites of the MOR catalyst for a substantial catalyst life were also discussed.

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2. Experimental

2.1. Preparation of catalysts

The H form MOR zeolites with Si/Al molar ratios of 5 and 10 were provided by the Catalysis Society of Japan. The MOR catalysts with different Si/Al molar ratios were prepared by dealumination treatments of MOR with Si/Al molar ratio of 10 with hydrochloric acid solutions of 0.05, 0.1, 0.5, 1 and 4 N. Samples of 5 g in hydrochloric acid solution of 200 ml were refluxed at 80 °C for 12 h. The filtered samples were washed with distilled water until the chloride ions could not be detected from the washing water by using a silver nitrate solution. The dealuminated MOR catalysts were dried at 120 °C for 5 h, and then calcined in air at 500 °C for 2 h.

The contents of silicon and aluminium in the dealuminated MOR catalysts were determined by using the EDX (NORAN Z-Max 3000 Series) attachment of the SEM (Jeol, JSM-5400). The Si/Al molar ratio average was taken from more than five analysis results. MOR catalysts were denoted as MOR(x) by writing the Si/Al molar ratio in parentheses. The aluminium contents on the external surface and in the bulk were compared with the XPS spectra which were recorded on a XPS (Surface Science 2701 MX-Probe). Al Kα radiation with a monochromator was used with working conditions of 10 kV and 8 mA. An analysis spot was 300 μm. The surface was sputtered by an Ar^+ beam with a sputtering rate of 0.5 Å s^{-1} (as SiO_2) which recorded the XPS spectra of the inside MOR particles.

2.2. Characterization of catalysts

The X-ray diffraction patterns of the MOR catalysts were recorded on a X-ray diffractometer (Rigaku D/MAX-1200) with a Cu Kα X-ray at 40 kV and 20 mA. Nitrogen adsorption isotherms were measured by a home-built volumetric adsorption apparatus at liquid-nitrogen temperature. MOR catalysts were dehydrated at 300 °C for 2 h prior to nitrogen adsorption. The surface area was calculated using the BET equation. Temperature-programmed desorption (TPD) profiles of ammonia from MOR catalysts were recorded to compare their acidic properties according to the method described elsewhere [24].

The uptake of o-xylene was measured using a quartz-spring gravimetric adsorption system. A sample was dehydrated at 300 °C under 1.33×10^{-4} Pa for 2 h. o-xylene (Hayashi Chemical, 99%) vapor was introduced to the sample at 120 °C, and the increase in the mass was recorded for 180 min.

The amounts of carbon deposited on the used catalysts were measured using a thermal gravimetric analysis system (TGA, DuPont Instrument, 951). Temperature increased in the air flow from 100 to 700 °C with a ramp of 10 °C min^{-1}. Used catalysts were washed with toluene using a Soxhlet apparatus to remove the non-reacted PE wax. Since the carbon deposited on the external surface departs easily compared to that in the pore during the washing treatment, the partial removal of the deposited carbon might make the measurement unreliable.

The catalytic activity of the external acid sites was compared by the cracking of 1,3,5-triisopropylbenzene (TIPB, Sigma, 99%). The molecular size of TIPB is larger than the pore entrance of the MOR, so the conversion of TIPB reveals the cracking activity of acid sites on the external surface [25]. A sample of 0.2 g was charged in a quartz tube reactor of a conventional flow microreactor and activated in a nitrogen flow at 550 °C for 30 min. TIPB cracking was carried out at 350 °C for 30 min. TIPB was introduced at the feed rate of 0.1 ml min^{-1} by a syringe pump (Keun-A, KAST005/150MT) and the products were collected using a collector buret cooled at 0 °C. The products were analyzed by a gas chromatograph (Donnm DS6200) with a DB-1 capillary column (0.53 mm × 30 m).

2.3. PE wax and its liquid-phase degradation

PE wax, a by-product of the polyethylene polymerization process, was provided by Daehan Petroleum Company. The liquid-phase degradation of PE wax was carried out using a batch reactor with a condenser, which enabled the separation of gas and liquid products from the reactor [12,13]. 10 g PE wax and 0.2 g catalyst were charged in a 100 ml three-neck flask. The amount of gas products was measured using an electronic flow-meter. The compositions of gas and liquid products were analyzed using a gas chromatograph (Donnam DS-6200) with a HP-1 column (0.2 mm × 50 m) and a FID detector.

3. Results and discussion

3.1. PE wax and its liquid-phase degradation

Elemental analysis (Vario EL) of the PE wax gave a ratio of hydrogen atom to carbon atom as 1.98, indicating that the PE wax was a saturated hydrocarbon with a small number of double bonds. The melting point was examined using a differential scanning calorimeter (DSC, DuPont Instrument 910), with a range of 82–110 °C. Absorption bands related to branched and aromatic hydrocarbons were not observed in the IR spectrum of the PE wax recorded on a FT-IR spectrometer (ATI Mattson, Genesis) with a resolution of 4 cm^{-1}. These results suggest that the PE wax used in this study, is a mixture of linear saturated hydrocarbons ranging from C_{40} to C_{80}. The content of branched or aromatic hydrocarbons was negligible in the PE wax, but a small number of double bonds was observed.

3.2. MOR catalysts with different Si/Al molar ratios

Five MOR catalysts with Si/Al molar ratios of above 12 were prepared by the dealumination of the MOR(10) catalyst. Molar ratios of the MOR catalysts used in this study ranged from 5 to 26. No remarkable differences in XRD patterns for all samples were observed, indicating the same crystalline structure. Surface areas were at the range of 410–450 $m^2\,g^{-1}$, and these values showed the maintenance of the pore structure even after the dealumination treatment.

Although the pore structure itself was maintained, the removal of aluminium at the pore entrance caused a slight increase in the pore size. The small change in the pore size by the dealumination may have induced the change in the diffusion rate of the MOR catalyst. The molecular size of *o*-xylene is very close to the pore size of MOR, so even a small change in the pore brings about a change in the uptake rate. The uptake curves of *o*-xylene on the MOR catalysts are shown in figure 1. The uptake rate at the initial stage increases with the increasing of the dealuminated extent of MOR catalysts. Aluminium atoms composing the skeletal of MOR zeolite are removed by hydrochloric acid, and thus the pore entrance increases slightly. But the asymptotic approaches of the uptake curves, regardless of the dealuminated extent, suggests similar pore volumes, indicating the maintenance of the original pore structure.

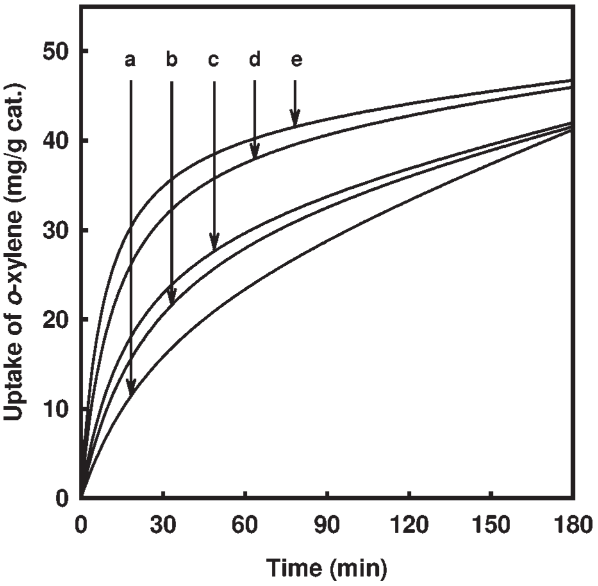


Figure 1. Uptake curves of *o*-xylene on the MOR catalysts at 120 °C: (a) MOR(5), (b) MOR(10), (c) MOR(12), (d) MOR(18), and (e) MOR(26).

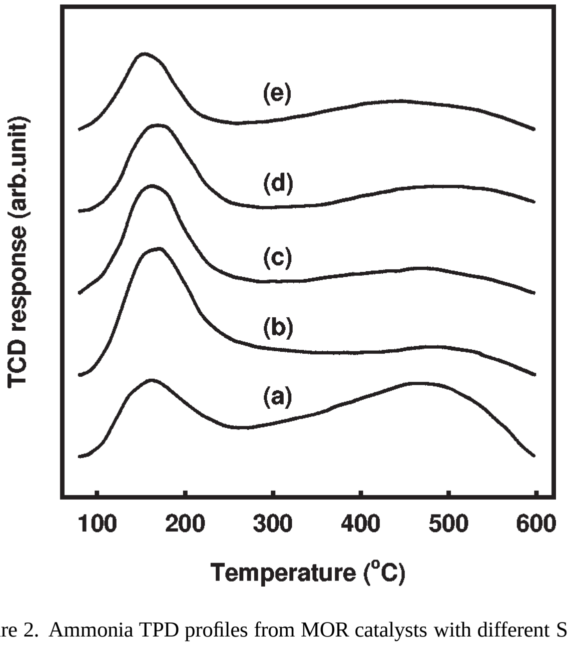


Figure 2. Ammonia TPD profiles from MOR catalysts with different Si/Al molar ratios: (a) MOR(5), (b) MOR(10), (c) MOR(12), (d) MOR(18), and (e) MOR(26).

The ammonia TPD profiles of the MOR catalysts are shown in figure 2. Two desorption peaks, one at 100–200 °C (l peak) and the other at 350–500 °C (h peak) were observed. The peak area of the h peak decreased with increasing Si/Al molar ratio, indicating the decrease of the number of strong acid sites. The differences in the temperatures at h peak maxima for all MOR catalysts are not considerable, so the acid strength of the strong acid sites does not change with the aluminium content.

3.3. Liquid-phase degradation of PE wax over MOR catalysts

PE wax was not thermally degraded to gas and liquid at 380 °C. The yield of gas products was only 3% of the thermal degradation even at 400 °C, and the formation of the liquid product was too small to measure quantitatively. In comparison, the total yield of the liquid-phase degradation of PE wax on the MOR(12) catalyst was about 65% at 380 °C. The degradation is significantly enhanced by using the MOR catalysts which lowers the cracking temperature and increases the yield. Figure 3 shows the degradation process of PE wax on the MOR(12) catalyst at 380 °C. At the initial stage, gas is mainly produced. When the temperature reaches 380 °C, the formation of a liquid product is predominant. The yield of the gas product is 25% and that

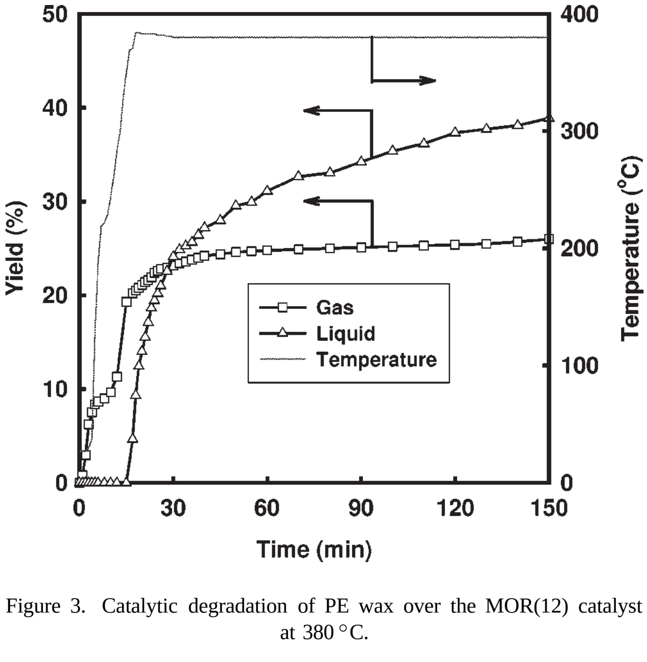
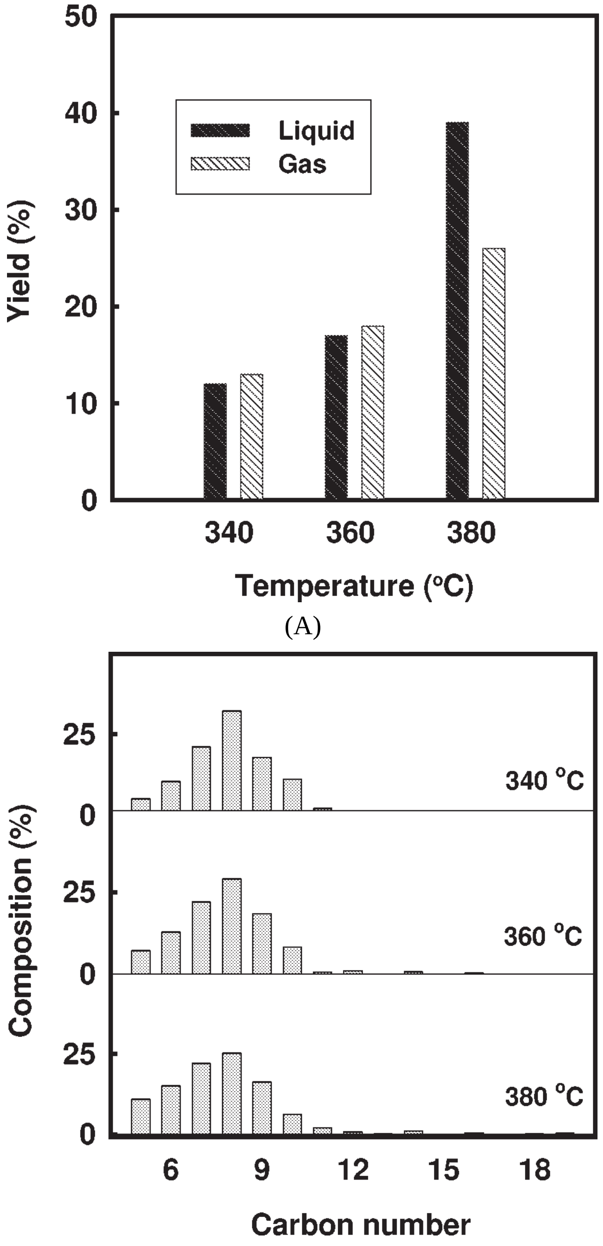


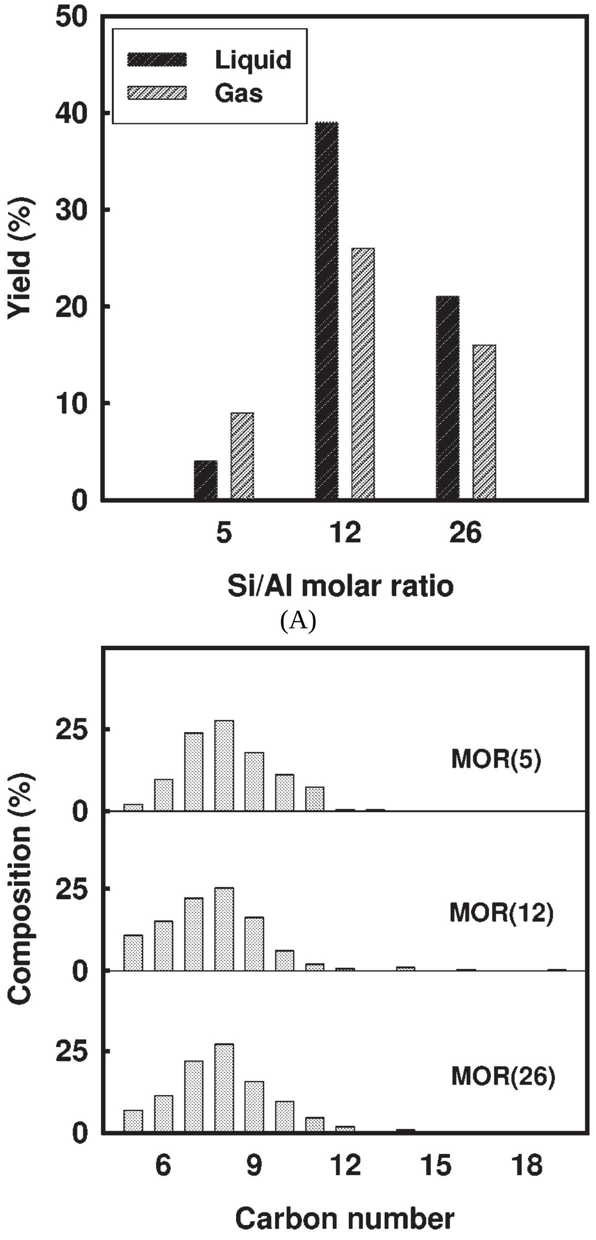
Figure 3. Catalytic degradation of PE wax over the MOR(12) catalyst at 380 °C.



(A)

(B)

Figure 4. Yields of gas and liquid products (A) and composition of liquid product (B) of PE wax degradation over the MOR(12) catalyst at various temperatures.



(A)

(B)

Figure 5. Yields of gas and liquid products (A) and composition of liquid product (B) of PE wax degradation over the MOR catalysts with different Si/Al molar ratios at 380 °C.

of the liquid product is 39% during the 150 min reaction time.

The behavior of the catalytic degradation of PE wax on the MOR catalyst varies with the reaction temperature. Figure 4 shows the yields of gas and liquid products, and the composition of liquid products obtained at the different reaction temperatures. The yields of gas and liquid products are low and similar to each other at 340 and 360 °C. A low thermal degradation was observed at 400 °C, so catalytic degradation experiments were carried out below 380 °C. The major components of the gas product were C_3–C_5 hydrocarbons. The product compositions were almost the same, although the reaction temperatures were different. The contents of C_7 and C_8 hydrocarbons are similarly high for all the liquid products, and the fraction of higher hydrocarbons than C_{12} was negligible. The fraction of C_5 hydrocarbons was slightly high at 380 °C, but the other compositions of the liquid products were almost the same. These findings mean that the catalytic degradation extent increases with increasing the reaction temperature, but the change in the reaction temperature does not induce any change in the degradation mechanism.

Since the catalytic degradation of PE wax occurs at the acid sites, the conversion and product composition are influenced by the Si/Al molar ratio of the MOR catalysts. As shown in figure 5, the yield of liquid products on

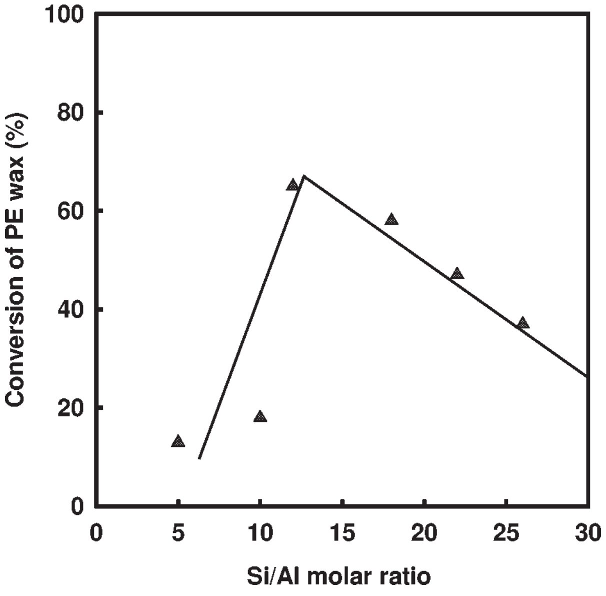


Figure 6. Effect of the Si/Al molar ratio on the conversion of PE wax in the catalytic degradation over the MOR catalysts at 380 °C.

the MOR(12) catalyst was high compared to those of the MOR(5) and MOR(26) catalysts. The conversion on the MOR(5) catalyst with a large content of acid sites was low, and that of the MOR(26) catalyst with a small content of acid sites was also low. The catalytic degradation ought to be slow on the MOR(26) catalyst because of its small number of acid sites. However, the poor catalytic activity of the MOR(5) catalyst was quite unexpected. The low conversion on the MOR(5) catalyst suggests that there is a negative effect of acid sites affecting the reaction process. The compositions of liquid products on the MOR catalysts are similar, even though their Si/Al molar ratios varied from 5 to 26. The fraction of small hydrocarbons of the liquid product on the MOR(12) catalyst was slightly higher than those of other catalysts, but the differences from other products were not remarkable. This means that the effect of the acid site amount on the composition of the liquid product is not significant, indicating no remarkable change in the degradation mechanism.

The fact that the Si/Al molar ratio is an important factor determining the extent of the catalytic degradation is obvious in figure 6. The conversion of PE wax, and the total yield of gas and liquid products, shows a volcano plot along the Si/Al molar ratio of the MOR catalysts. The maximum conversion was obtained on the MOR(12) catalyst, whose aluminium content was not as high as that of the MOR(5) catalyst and was not as low as in the MOR(26) catalyst. This plot suggests that a high concentration of acid sites inhibits the degradation reaction, resulting in a low conversion over the MOR(5) and MOR(10) catalysts.

The slow uptake rate of *o*-xylene (figure 1) may be considered as a plausible cause for the low conversion on the MOR(5) catalyst. But this explanation has a low feasibility, because the compositions of the liquid products are similar regardless of the variance of the Si/Al molar ratio. If the restriction in the pore entrance was the main factor to reduce the conversion on the MOR(5) catalyst, the production distribution should be different with that of the MOR(26) catalyst.

Table 1
The Si/Al molar ratios of MOR(5) and MOR(12) catalysts determined from XPS spectra.

Catalyst	Without sputtering	After being sputtered for 35 s[a]
MOR(5)	4.0	5.5
MOR(12)	13.7	12.5

[a] The sputtered depth is estimated to be about 20 Å.

The other possible explanation for the low conversion on the MOR(5) or MOR(10) catalyst is the faster deactivation than for MOR catalysts with Si/Al molar ratios of above 12. Since most of the primary cracked products were unsaturated hydrocarbons, a high concentration of olefinic products was obtained in the catalyst with a high concentration of acid sites at the initial reaction stage. Adsorbed and activated olefinic molecules are easily oligomerized to large molecules, which deposit on the catalyst surface.

The Si/Al molar ratios of MOR(5) and MOR(12) catalysts measured from the XPS spectra are listed in table 1. The Si/Al molar ratio on the external surface of the MOR(5) catalyst was lower than that of the bulk, indicating a high concentration of acid sites on the external surface. The Si/Al molar ratio of MOR(5) became greater than that of the external surface after sputtering for 35 s. Sputtering of 35 s corresponds to about the depth of 20 Å. These findings mean that the concentration of acid sites on the external surface of the MOR(5) catalyst is higher than the other part. Likewise, the Si/Al molar ratio on the external surface of the MOR(12) catalyst was higher than that of the bulk. The Si/Al molar ratio of the MOR(12) catalyst became smaller than that of the external surface after sputtering for 35 s. These facts indicate that aluminium atoms of MOR zeolite are preferentially extracted from the external surface by dealumination.

Although the amount of carbon deposition can be measured from the mass reduction by burning, as recorded in TG curves in the atmosphere, it is hardly possible to distinguish the mass reduction from the non-reacted PE wax and carbon deposition. If the non-reacted PE wax was completely removed from the used catalysts by solvent extraction, the mass reduction in the TG curve would correspond to the amount of carbon deposition. Figure 7 shows the TG curves of the MOR catalysts used at 380 °C for 150 min. The mass reduction from 450 to 700 °C corresponded to carbon deposition, because the non-reacted PE wax was removed below 450 °C. The mass reduction does not show any proportional relationship with the conversion of PE wax. The lowest active MOR(5) catalyst showed a small amount of carbon deposition. The amount of carbon deposition increased with increasing the Si/Al molar ratio of the MOR catalysts. These facts mean that the amount of carbon deposition is not simply related to the catalytic ac-

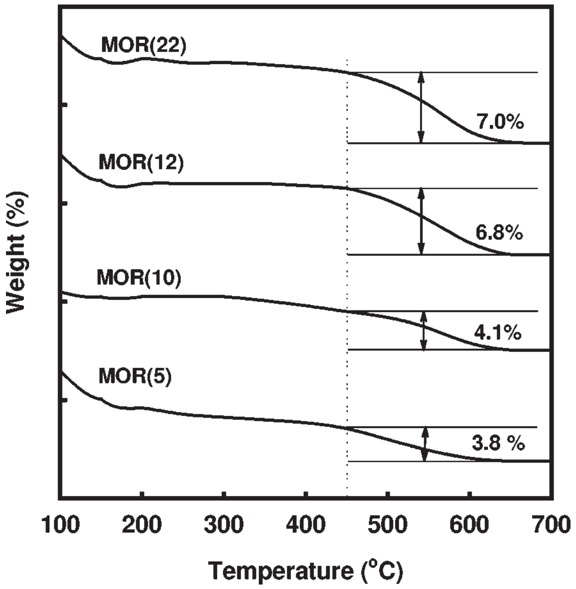


Figure 7. TG curves of used MOR catalysts in the catalytic degradation of PE wax at 380 °C for 150 min.

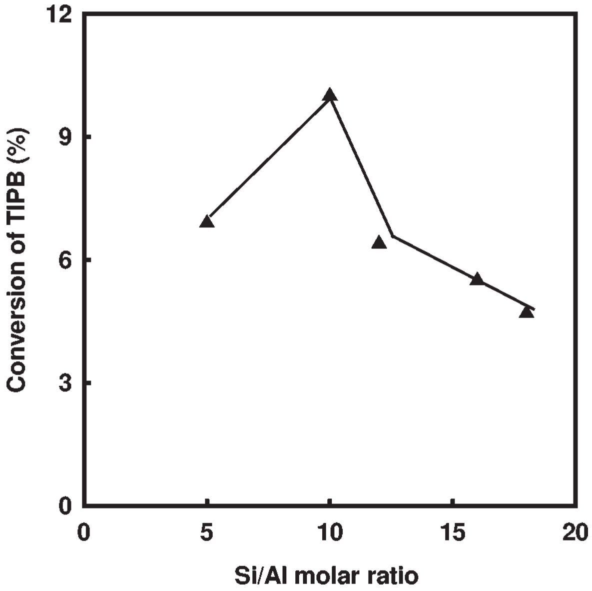


Figure 8. Effect of Si/Al molar ratio on the conversion of TIPB over the MOR catalysts at 350 °C.

tivity. On the contrary, if the carbon is largely deposited on the catalyst with a high concentration of acid sites, the low conversions of PE wax on the MOR(5) and MOR(10) catalysts are caused because of pore blocking by the carbon deposition. The preference of oligomerization allows the easy formation of carbon deposition on the external surface. The pore blocking by the carbon deposited on the external surface could not be confirmed by a nitrogen adsorption isotherm, because a small loss of carbon deposited on the external surface gives a relatively large variance in the surface area compared to those deposited in the pore. Though the mass reduction on the MOR(5) catalyst is small, the intense formation of carbon deposition on the external surface resulted in severe pore blocking. Therefore, the MOR(5) and MOR(10) catalysts with a large amount of acid sites showed low conversions compared to the MOR(12) catalyst, because of fast deactivation by pore blocking. The optimum Si/Al molar ratio of the MOR catalyst for the liquid-phase degradation of polymeric materials should be determined by the concentration of acid sites to minimize carbon deposition, as well as the amount of acid sites to achieve high catalytic activity.

The amount of acid sites on the external surface of zeolite with a small pore was confirmed by the TIPB conversion [25]. Figure 8 shows the effect of the Si/Al molar ratio on the conversion of TIPB over the MOR catalysts. The conversion of TIPB shows also a volcano plot along the Si/Al molar ratio of the MOR catalysts, in a similar manner as figure 6. In practice, the TIPB conversions of MOR catalysts should decrease with increasing the Si/Al molar ratios. However, the MOR(5) catalyst exhibited lower activity than the MOR(10) catalyst, because the carbon deposition was severe on the external surface of the MOR(5) catalyst with a large amount of acid sites. Figure 8 shows that the amount of acid sites is not always related to the catalytic activity of the MOR catalyst in the acid-catalyzed reaction, because a large amount of acid sites also accelerates the carbon deposition inducing the severe deactivation as shown in the liquid-phase degradation of PE wax and the TIPB cracking.

4. Conclusion

The variation of the conversion of PE wax with the Si/Al molar ratio of the MOR catalyst in the liquid-phase catalytic degradation shows a volcano plot. The maximum conversion indicates two different trends in the conversion with the amount of acid sites. Acid sites are responsible for the catalytic degradation, but they also accelerate carbon deposition. The fast formation of carbon deposition on the MOR catalyst with a high concentration of acid sites causes low conversion of the liquid-phase catalytic degradation. Since the carbon deposition is severe in the liquid-phase degradation compared to the gas-phase reaction, the Si/Al molar ratio of the MOR catalyst is carefully controlled to obtain a high degradation activity and a substantial catalyst life.

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