Catalytic Degradation of Polyethylene and Polypropylene to Fuel Oil

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Abstract: Thermal and catalytic degradation of plastic polymers, polyethylene and polypropylene to fuel oil were carried out in batch operations. The catalysts employed were acid silica-alumina (SA-1, SA-2) and zeolite ZSM-5, and non-acidic mesoporous silica FSM (folded sheet material). The yields of product gas, liquid and residues, recovery rate of liquid products, and boiling point ranges of liquid products due to degradation were compared with those of non-catalytic thermal degradation. Both the effect of catalytic contact mode and of catalyst type on the degradation were studied.

In liquid-phase degradation of PP over SA-1, liquid hydrocarbon products were obtained in a yield of 69 wt.-% with a boiling point range 36-270 °C, equivalent to the boiling point of normal paraffins C6 - C15. The liquid products from catalytic degradation have a carbon-number distribution very similar to commercial motor gasoline. In vapor-phase contact, the yield of liquid products was much lower (54 %) and the rate of liquid recovery was much slower.

With FSM, the initial rate of degradation of PP and PE to liquid products was as fast as that over acid catalyst SA-1, but the yield of liquid products was higher. The liquid products from catalytic degradation over FSM have a carbon-number distribution similar to kerosene and diesel oil. In repeated use, SA-1 deactivated very rapidly due to coke deposition on the catalyst, whereas FSM deactivated much more slowly. These findings suggest that mesopores surrounded by the silica sheet may act as reservoir for radical species, which accelerate the degradation of plastic melt.

INTRODUCTION

There have been many reports on the catalytic degradation of plastic polymers over solid acid catalysts aiming at the conversion of waste plastics to liquid hydrocarbons (Refs 1-4). From the type of the reaction apparatus and the method of operation used in these studies it is not clear which steps of the thermal degradation process the solid catalyst acts on. Uemichi et al. (Refs 1,2) conducted the degradation of polypropylene (PP) at 420-550 °C in a flow-type reactor using solid acid catalysts, so that the gaseous hydrocarbons were predominant in the products. Saito (Ref. 3) reported a two-step polyethylene (PE) degradation process: thermal degradation using a natural zeolite at 450 °C followed by the degradation with a synthetic zeolite at 300 °C. In the first step of the catalytic degradation, a wax-like product (C5-C43)

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was obtained in 87 wt.-% yield, whereas the other produced liquid hydrocarbons in an overall yield of 74 wt.-%. Degradation of PE with silica-alumina reported by Ohkita et al. (Ref. 4) was actually catalytic cracking of volatile compounds in the thermally degraded at 400 °C. In order to investigate catalytic steps in polymer degradation, the present work compares catalytic effects in polypropylene (PP) degradation, when the melted PP was brought into contact with solid catalysts (liquid-phase contact) and when the thermally degraded hydrocarbon vapors from PP were brought into contact with solid catalyst particles (vapor-phase contact) (Fig. 1).

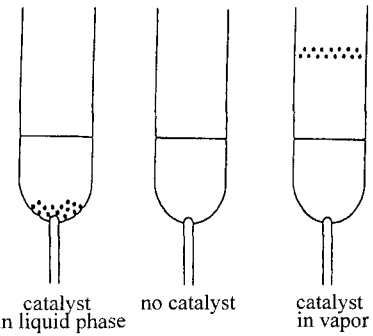

Fig. 1 Catalytic contact mode in plastic degradation

In order to investigate the effects of the catalyst type on plastic degradation, catalytic degradation of PE over various types of solid acid catalysts, such as silica-alumina, zeolite and non-acidic mesoporous silica (FSM), have been investigated. The yields of product gas, liquid and residues, the recovery rate of liquid products, and the boiling point distribution of liquid products were compared with those of non-catalytic thermal degradation.

EXPERIMENTAL

PP pellets (4.0 mm in size) were obtained from UBE Chemical Industries and PE (high-density, HDPE) from Mitsui Petrochemical Co. Ltd. The catalysts employed in this study were silica-alumina (SA-1, SA-2), zeolite ZSM-5 and mesoporous silica (KFS-16B). Silica-alumina SA-1 (molar ratio SiO_2/Al_2O_3 83.3/16.7) and SA-2 (SiO_2/Al_2O_3 21.1/78.9) were commercial with a surface area of 420 and 270 m^2/g, respectively. Zeolite ZSM-5 was prepared in our laboratory by the procedure described in a patent (Ref. 5); its molar SiO_2/Al_2O_3 was 97.7/1.3 and the surface area 360 m^2/g. Mesoporous silica was prepared using colloidal silica having a composition of 30.5 wt.-% SiO_2, 0.4 wt.-% Na_2O and 69 wt.-% H_2O, by the procedure described by Inagaki et al. (Ref. 6); its surface area was 900 m^2/g.

Thermal degradation of the polymer was carried out in a glass reactor (35 mm i.d., 350 mm length) under atmospheric pressure in a batch operation. Figure 2 shows the schematic diagram of the experimental apparatus used in this study.

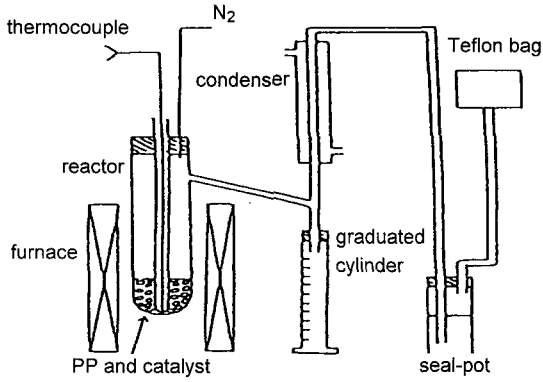

Fig. 2 Experimental set-up

10 g of polymer pellets was loaded into the reactor for thermal degradation and 10 g of plastic polymer mixed with 1.0 g of catalyst (average size 1.0 mm) was loaded into the reactor for the catalytic degradation (liquid-phase contact). For vapor-phase catalytic degradation, catalysts were placed on a stainless steel netting, 10 cm from the bottom of the reactor. In a typical run, after the reactor was charged, the air remaining in the reactor was purged with N_2 at a flow rate of 30 ml/min. The reactor was then heated to 120 °C in 60 min (1.7 °C/min) and held at 120 °C for 60 min in order to expel the adsorbed water from the catalyst and PP. Nitrogen flow was then cut off and the temperature was increased from 120 °C to the degradation temperature at a rate of 3 °C/min. The degradation products were separated into three groups: gases (products not condensable with water), liquid hydrocarbons and residues. The experimental run was stopped when no liquid drop came out from the reactor for the last 30 min. The amount of gaseous products was determined by subtracting the weight of liquid products and residues from the plastic feed. The term residue refers to both the carbonaceous and waxy matter remaining in the reactor after the degradation run. Liquid and gaseous products of degradation were analyzed by gas chromatography with an OV-101 capillary column and a Porapak QS column, respectively.

RESULTS AND DISCUSSION

Effect of contact mode on polypropylene degradation

The yields of product gases, liquids and residue obtained from the thermal and catalytic (liquid- and vapor-phase contact) degradation of PP at 380 °C are shown in Table 1.

Table 1 Product yields[a] (wt-%) and properties for thermal and catalytic degradation of polypropylene at 380 °C

Product	Non-catalytic	Catalytic[b]	
	(thermal)	vapour phase	liquid phase
Liquid (L)	64.9	54.5	68.8
Gaseous (G)	24.7	35.0	24.8
Residue (R)	10.4	10.5	6.4
Bromine number[c]	66.7	90.3	94

[a] G = 100 - (L + R); [b] silica-alumina; [c] g Br_2/100 g liquid

For catalytic degradation in vapor phase, the yields of residue did not differ significantly from those in thermal degradation, the yields of liquid products being lower and those of gaseous products higher. These results imply that in vapor phase, thermally degraded hydrocarbons underwent further decomposition to gaseous products over the silica-alumina catalyst. On the other hand, for catalytic degradation in liquid phase, the yields of gaseous products did not differ much from those of thermal degradation, but the yields of liquid products increased at the expense of the residue yield. As shown in Fig. 3, gaseous products from the catalytic degradation mainly consisted of butenes (57 wt.-%) and propylene (30 wt.-%), whereas the gaseous products from thermal degradation consisted of propylene (70 wt.-%) and ethane (28 wt.-%). The above results indicate that in the liquid-phase contact, the waxy residues (heavier hydrocarbons) decomposed to lighter liquid hydrocarbons over the silica-alumina catalyst, which resulted in higher yields of liquid products than in the case of thermal degradation.

Figure 4 shows the cumulative volume of liquid products and the temperature in the reactor as a function of time. The time started with the heating of the sample from 120 °C to the reaction temperature. The initial rate of liquid-phase degradation of PP over the silica-alumina catalyst was 1.2 g products/g residual liquid.h, which is about four times greater than that of the non-catalytic thermal degradation and catalytic degradation in vapor phase. These results suggest that acid sites of silica-alumina in contact with the PP melt significantly accelerated the degradation of PP. In separate experiments on thermal and catalytic (liquid-phase) degradation of PE revealed that in catalytic degradation, when PE was heated at 430 °C, the molecular weight distribution (GPC) of the residual liquid in the reactor was shifted to a lower molecular-weight range than that in thermal degradation (Ref. 7). This result also indicates that the solid acid catalyst in direct contact with the melted polymers promotes their degradation to lower-molecular-weight compounds.

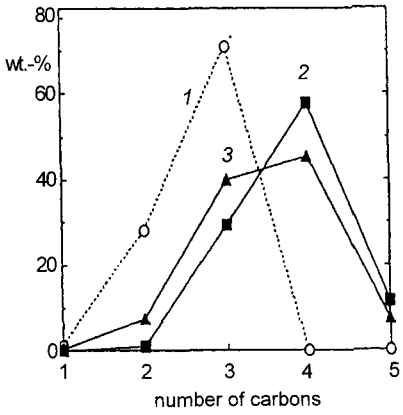

Fig. 3 Distribution of the carbon number of in the gaseous product from degradation of PP at 380 °C

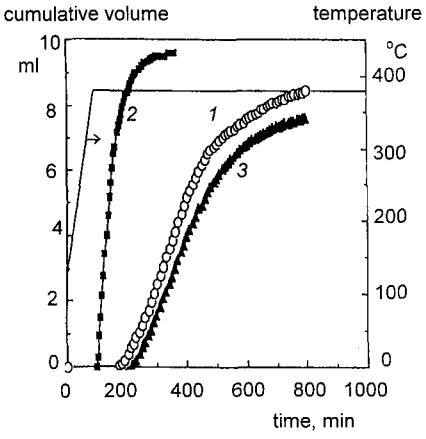

Fig. 4 Cumulative volume of the liquid product

1 non-catalytic (thermal), *2* catalytic in liquid phase, *3* catalytic in vapor phase

The liquid products were characterized by a normal-paraffin-gram (NP-gram) proposed by Murata et al. (Ref. 8) Figure 5 shows the NP-gram (carbon number distribution) of liquid products obtained from catalytic and thermal degradation of PP at 380 °C. The carbon numbers on abscissa in Figure 5 were obtained by analyzing gas chromatograms of the liquid products. These carbon numbers are equivalent to retention values of the corresponding normal paraffins and indicate the distribution range of boiling points of hydrocarbons.

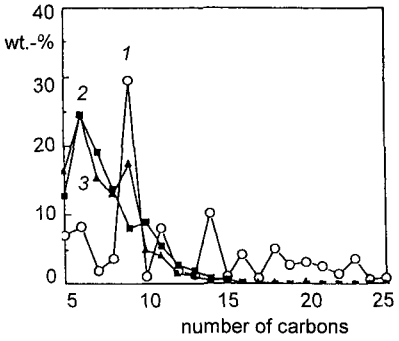

Fig. 5
NP-grams of liquid product from thermal and catalytic degradation of PP at 380 °C (for numbering of curves, see Figs 3 and 4)

In thermal degradation, the liquid hydrocarbon products were distributed in a wide range of equivalent hydrocarbons with boiling points ranging over 36-405 °C (C5-C25). Murata et al. (Ref. 8) have reported a similar result for the thermal degradation of PP at 390 °C,

characterized with comb-like peaks at *n*-C6, *n*-C9, *n*-C11, *n*-C14 and *n*-C16, etc. On the other hand, in the PP degradation over silica-alumina with both the liquid and vapor phase contact, the liquid products were predominantly equivalent to *n*-C5 – *n*-C15 hydrocarbons with boiling points ranging over 36-270 °C. The bromine number of the liquid products was determined in order to compare the degree of total unsaturation in liquid products from the thermal and catalytic degradation of PP (see Table 1). Bromine numbers of liquid products were 66.7 and 90-94 (g Br/100 g product) for thermal and catalytic degradation, respectively, indicating that the catalytically degraded products have a higher degree of total unsaturation than the non-catalytic, thermally degraded products. On the basis of these results, we suggest that the silica-alumina (solid acid) catalyst breaks the long polymer chain into small units, starting from the ends. As a result, the amount of unsaturated hydrocarbons increases in the product. It is well known that thermal degradation of polyolefins occurs by random scissoring long polymer chains and the products of degradation are distributed in a wide range of molecular weights. Therefore, the amount of total unsaturation per gram of liquid products is lower for thermal degradation than for catalytic degradation.

On the basis of the above results, we suggest the following macroscopic degradation model for plastic degradation (Fig. 6). The molten polymer first degraded thermally to visbreaking oil and then to liquid and gaseous hydrocarbons and a solid residue. The solid acid catalyst promotes the degradation of the visbreaking oil to light fuel oil in the second step.

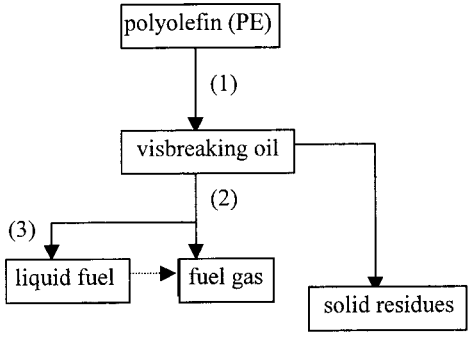

Fig. 6
Macroscopic degradation model of polyolefin plastics

Effect of catalyst type on polyethylene degradation

The product yields for thermal and catalytic degradation of HDPE performed at 430 °C are shown in Tables 2 and 3.

Table 2 Product yields (wt.-%) and properties for thermal and catalytic degradation of high-density polyethylene at 430 °C [a]

Products	Thermal	SA-1	SA-2	ZSM-5	KFS-16B
Liquid	69.3	67.8	74.3	49.8	71.1
Gaseous	9.6	23.7	13.4	44.3	11.0
Residue	21.1	8.5	12.3	5.8	17.9
Liquid products					
Density (g cm^{-3})	0.76	0.72	0.74	0.72	0.74
Average carbon number	11.9	7.6	9.0	8.5	9.8
Bromine number [b]	58.0	96.1	90.0	113.0	113.0

[a] 10 g of both HDPE and catalyst used; [b] g Br_2/100 g liquid.

Table 3 Product yields (wt-%) and properties for degradation of high-density polyethylene at 430 °C using repeatedly KFS-16B as a catalyst [a]

Products	Run 1[c]	Run 2[c]	Run 3[c]	Run 4[c]	Run 5[c]
Liquid	71.1	81.4	80.1	81.9	75.2
Gaseous	11.0	10.1	9.2	9.3	8.9
Residue	17.9	8.5	10.7	8.8	15.9
Liquid products					
Density (g cm^{-3})	0.74	0.75	0.76	0.76	0.76
Average carbon number	9.8	12.2	14.0	14.4	12.5
Bromine number [b]	113.0	80.0	58.0	56	73

[a] 10 g of both HDPE and catalyst used; [b] g Br_2/100 g liquid; [c] The catalyst was calcined in air at 600 °C for 3h

In catalytic degradation, two types of silica-alumina, SA-1 and SA-2 (having different SiO_2/Al_2O_3 molar ratios), zeolite ZSM-5, and mesoporous silica FSM were used as catalysts. The acidity (strength) of these catalysts was investigated by the temperature-programmed desorption (TPD) of NH_3. NH_3-TPD results shown in Fig. 7 revealed that the acidity of these catalysts decreases in the order SA-1 > ZSM-5 > SA-2 >> FSM = 0. Thus, mesoporous silica (FSM) possesses virtually no acidity. In Table 1 (left half), silica-alumina catalyst SA-2 of moderate acidity produced the largest amount of liquid products. ZSM-5, possessing strong acid sites, produced less liquid and more gaseous products than the other acid catalysts (SA-1, SA-2). These results are in agreement with the fact that strong acid catalysts catalyze degradation/cracking of heavier hydrocarbons to lighter or gaseous hydrocarbons than weak-acid catalysts. In thermal degradation, the yield of liquid products was ca. 69 wt % and that of the residue, 21 wt.-%. On the other hand, FSM, having no acid sites, produced liquid hydrocarbons in a yield of more than 71 wt.-% and the yield of residue was much lower than that in non-catalytic thermal degradation (Ref. 9).

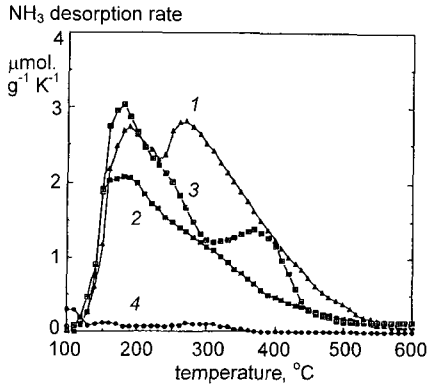

Fig. 7 NH_3-TPD spectra of the catalysts

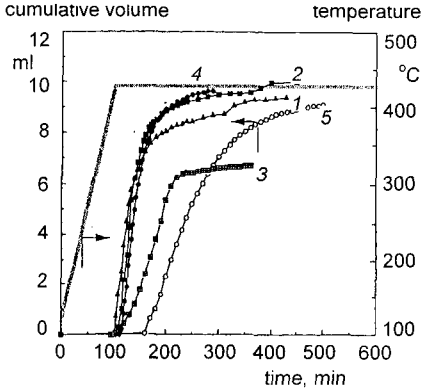

Fig. 8 Cumulative volume of liquid product from from degradation of HDPE at 430 °C

1 SA-1, *2* SA-2, *3* ZSM-5, *4* KFS-16B, *5* thermal

Figure 8 shows the cumulative volume of liquid products and the temperature in the reactor as a function of the elapsed time. As can be seen, the rate of degradation of HDPE over solid acid catalysts is much faster than that of the thermal degradation. Surprisingly, over mesoporous silica (FSM), which contains no acid sites, the rate of HDPE degradation was also faster than non-catalytic thermal degradation and comparable with that over solid acid catalysts (SA-1, SA-2). These results suggest that mesoporous silica FSM, having a uniform hexagonal pore of 3.6 nm, accelerated the degradation of HDPE, even though the FSM catalyst does not contain any significant acid sites.

The yields of gaseous products in HDPE degradation are shown in Table 2, while Fig. 9 shows their composition. In thermal degradation, the gaseous products were mainly C3 (propane, propylene), C2 (ethane, ethylene) and a small amount of C4 (butane, butenes). In catalytic degradation over SA-1, SA-2, ZSM-5 and FSM, the content of C2 and C3 hydrocarbons decreased and that of C4 and C5 increased significantly. Previously we reported (Ref. 7, 10) that the decrease in C2 and the increase in C4 hydrocarbons in gaseous products is a specific feature of the solid acid-catalyzed degradation of PE.

Composition of the liquid products from HDPE degradation is shown in Fig. 10. In thermal degradation, the liquid products were distributed in a wide range of carbon numbers (*n*-C5 to *n*-C22), equivalent to boiling point ranges of 36-370 °C.

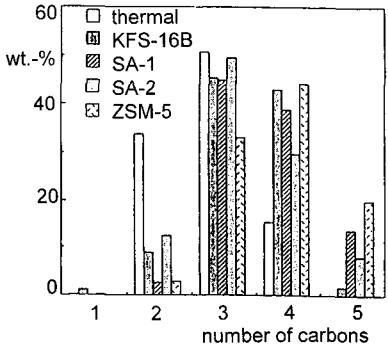

Fig. 9 Composition of the gaseous product from degradation of HDPE at 430 °C

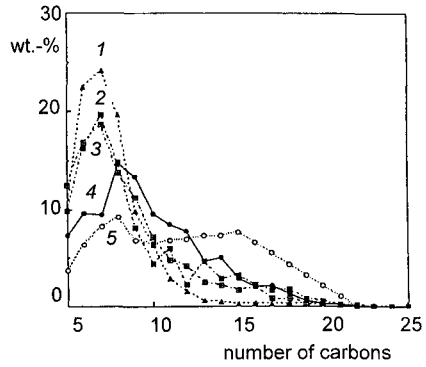

Fig. 10 NP-grams of the liquid product from thermal and catalytic degradation of HDPE at 430 °C (for numbering of curves, see Figs 7 and 8)

In catalytic degradations over SA-1, SA-2 and ZSM-5, the weight fraction of light hydrocarbons (C4 - C10) increased and that of heavier hydrocarbons (> C12) decreased. The carbon number distribution of liquid products from catalytic degradation over SA-1 was very similar to commercial motor gasoline fractions. Quantitative analysis of the oil fraction for aliphatics, olefins, diolefins and aromatics was not carried out. However, qualitative analysis of the liquid products by IR spectroscopy revealed the following: the oil obtained from thermal degradation contained both paraffins and olefins, but no aromatics. Degradation oil from catalytic degradation over SA-1 contained more olefins than the thermal-degradation oil and much less aromatics than in the catalytic degradation over ZSM-5. The liquid products from degradation over FSM were much lighter than the thermal degradation products but heavier than the solid-acid catalytic degradation products as shown in Fig. 10 and also indicated in Table 2 by the average carbon number of the liquid products. For FSM, the bromine number of the liquid products was also similar to that in thermal degradation. From a comparison of the composition of kerosene and diesel oil as evaluated by NP-gram, it follows that the liquid products from degradation over FSM contain mainly kerosene and diesel fraction oil. As a fuel for boilers or oil-fired furnaces, kerosene and diesel fraction are more desirable than the gasoline fraction as they are easy to handle. Compared with the non-catalytic thermal degradation, FSM not only accelerates the rate of degradation of HDPE but also degrades heavier waxy compounds to kerosene or diesel fraction hydrocarbons.

Life test or stability test of FSM in HDPE degradation was performed by repeating batch operation using the same catalysts in four consecutive runs. The yields of products are shown in Table 2 (right-hand side). The results of the first run with the fresh catalyst were mentioned earlier. In the second through fourth run, the yields of liquid products were more than 80 %. It is interesting to note that after the first run, the colour of the catalyst remained almost white, i.e., no coke formation was observed. In contrast, with solid acids SA-1, SA-2 and ZSM-5, the catalysts turned black after the first run due to the formation of coke. With FSM, even after four consecutive runs, the colour of the catalyst was off-white or light brown.

Figure 11 shows the cumulative volume of liquid products from FSM for repeated runs compared with that from non-catalytic thermal degradation. The rate of degradation of HDPE decreased slowly after repeated use of the catalysts, indicating slow deactivation of the catalysts. However, the rate of degradation even in the fourth run was faster than the thermal degradation. After the fourth run, the catalyst was regenerated by burning off the coke in air (calcination) at 600 °C for 3 h. The rate of degradation of HDPE over the regenerated catalyst was the same as in the second run. We performed similar life-test experiments with SA-1 for the degradation of PP at 380 °C. The rate of degradation of PP to liquid products decreased drastically in consecutive runs and in the fourth run, it almost decreased to that of the thermal degradation (Ref. 11) These results indicate that due to strong acid sites in SA-1, the coke deposited on the catalyst results in a drastic deactivation by covering the active site of the catalyst surface.

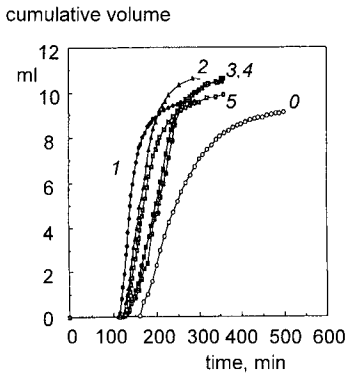

Fig. 11
Life test of KFS-16B catalyst by repeated degradation runs of HDPE at 430 °C (*0* thermal, *5* regenerated, *1-4* 1st, 2nd, 3rd, 4th run)

Figure 12 shows the mechanistic aspects of PE and PP degradation with solid catalysts. Generally, the mechanism of their degradation over solid acid catalysts is considered similar to the carbonium ion mechanism proposed for hydrocarbon cracking over solid acid catalyst.

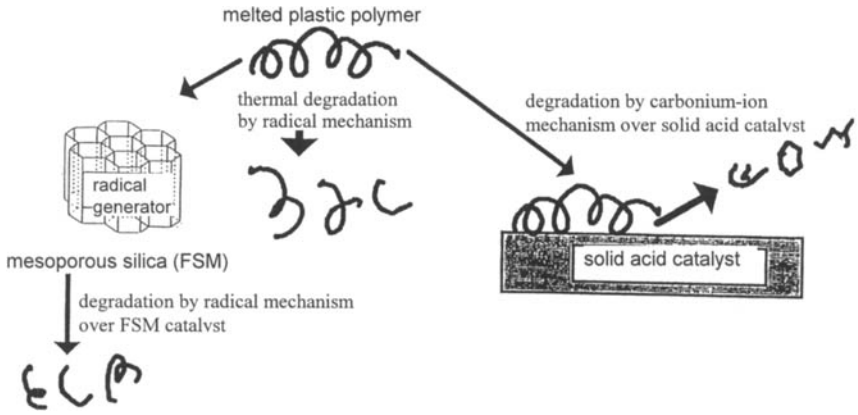

Fig. 12 Mechanistic aspects of polymer degradation over solid catalysts

Although the FSM catalyst does not contain any acid site, it accelerates the degradation rate of PE significantly. It seems likely that the degradation mechanism of polyolefin over FSM is deeply associated with the specific feature of the hexagonal large pore structure of the catalyst but not with the acid sites. A recent study (Ref. 12) of the methacrylate polymerization using mesoporous zeolites (MCM-41, FSM-16, MCM-48) demonstrated that the restricted pores of these materials act as nanometric reactor vessels where the radicals persist longer than in the conventionally used solution medium, resulting in the production of polymers with high molecular weights. Similarly, the acceleration of degradation of PP and PE over mesoporous silica (FSM) observed in this study can be explained by long persistance of the radicals produced by thermal degradation of polymers in the pores of FSM, which accelerates the degradation. This "radical flask" concept explicitly explains our findings from the polymer degradation using FSM, viz. acceleration of degradation and a product distribution similar to the thermal degradation.

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