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Catalytic transformation of the gases evolved during the thermal decomposition of HDPE using acid-activated and pillared clays

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HDPE was thermally decomposed in a thermobalance and the evolved gases were passed through a bed of catalyst. Two acid activated clays of different structure were used, *i.e.* sepiolite (SEP), which is a fibrous clay mineral, and smectite (K10) which is a layered mineral. In addition two pillared smectites were studied one which was pillared with an Al species (AZA) and the other with an Al/Fe-species (FAZA). The thermal and catalytic decomposition of HDPE was studied under dynamic (35 to 650 °C at 10 °C $\min^{-1}$) and isothermal (60 min at 420 °C) conditions. The evolved gases were analysed using TG–OTM–GC–MS. The thermal decomposition of HDPE yielded characteristic quartets of peaks assigned to *n*-alkanes, alk-1-enes, alk-*x*-enes and α,ω-dienes in the range C_4–C_{20}. Species of higher molecular weight than C_{20} were not detected. All four catalysts converted the alkenes present in the thermally generated off gases into light gases and aromatic species including respectable quantities of toluene, xylenes, tri- and tetra-methylbenzenes. Ethylbenzenes and naphthalenes were produced to a lesser extent. AZA and FAZA produced the largest yield of aromatics and sepiolite is considered to produce significant quantities of low molecular weight gases in the isothermal process. The product distribution over sepiolite suggested that there were fewer dehydrocyclisation sites on this catalyst. None of the catalysts used was capable of cracking the saturated alkanes.

Waste polymers are presently disposed of using one of three methods, landfill, incineration or recycling.[1] Not only is the chemical content of the polymer lost during two of these processes but all three present environmental problems. The slow kinetics of degradation together with the low weight-to-volume ratio of the polymers makes landfilling an unacceptable option,[2] whilst incineration yields a variety of products any one of which may present an environmental hazard. Consequently, thermal methods of recycling polymers have received considerable attention and the possibility of recovering high-value products has been assessed. For example, Uddin *et al.*[3] reported that the products from the thermal pyrolysis of polyethylene included alkenes and saturated hydrocarbons (n-C_2–n-C_{25}) with a broad distribution, whereas McCaffrey *et al.*[4] identified a mixture of straight chain alkanes and alkenes, with an average chain length of 13.2–14.5 carbons. Neither group reported a significant amount of aromatic species.

Catalytically assisted polymer pyrolysis is an attractive method of recycling because it offers a number of benefits including reduced operating temperatures and evolution of high value products,[3] a reduction in the number of products evolved[5] and an increase in the rate of polymer decomposition.[1] Two distinct methods of catalytic pyrolysis are used, (1) mixing the polymer and catalyst together to obtain an intimate physical contact between the two[1–9] or (2) directing the thermal decomposition products over a catalyst which is physically distant from the polymer.[10–13] Most catalytic investigations have been conducted under nitrogen but studies involving hydrogen[2,8] and high pressures[8] are beginning to emerge. Heating polymer/catalyst mixtures changes both the nature and the distributions of species evolved during pyrolysis.[3,5] In the presence of a silica-alumina catalyst, Uddin *et al.*[3] observed a narrower distribution of hydrocarbons (n-C_2–n-C_{15}), whilst Uemichi *et al.*[5] reported the presence of *n*-alkanes, isoalkanes, alkenes and aromatics. In the latter case the distribution of alkanes spanned a very narrow range (C_3–C_5) and the aromatics made up a significant portion of the total amount of products evolved.

Numerous catalysts have been evaluated, notably zeolites[2,6,7,9–12] and silica-alumina mixed oxides.[3,5,6,9,10,13] In contrast, clays and pillared clays, which represent a convenient, cheap and widely available alternative to expensive manufactured catalysts, have received no attention. A major disadvantage in the use of clays as catalysts is that their potentially extensive surface area is not available at temperatures in excess of 150–200 °C because the sorbed interlamellar molecules are driven off and the layers come into direct contact with each other forming a collapsed clay. Early attempts to overcome this unfortunate property centred on acid leaching of the octahedral sheet which increased both the surface area and the available acidity sufficiently for them to be used as cracking catalysts in the petroleum industry.[14] More recently the surface area and porosity at high temperatures ($\leqslant$500 °C) have been controlled by the introduction of polyoxymetal cations into the interlayer region which, when the composites are fired, form rigid, thermally stable pillars.[15] These pillared clays are microporous, have surface areas approaching 300 $m^2\ g^{-1}$, remain expanded up to 500 °C and make useful acid catalysts.[16] By contrast, sepiolite is a hydrated magnesium silicate wherein the 2 : 1 structure described above forms laths which are joined together at the edge.[17,18] This results in a fibrous mineral in which channels (5.6 × 11.0 Å) run the whole length of the fibre axis. Polar molecules such as alcohols, acetone and olefins are able to penetrate deeply into the channel network.[19] However, at temperatures near 250 °C the structure and the channel dimensions are reduced. Nonetheless, the accessible surface[20] and acidity[21] of sepiolite also responds favourably to acid-leaching and the resulting product can be used as an acid catalyst.[22]

Evaluation of the technical constraints and the relative sizes of the markets for different polymers have identified high density polyethylene HDPE and polyethylene terephthalate PET as the most realistic focus for catalytic conversion into useful products.[23] In the present study the distributions of the secondary cracking products obtained when the thermal degradation products from HDPE were passed over pillared clays (AZA and FAZA) and acid treated clays (K10 and Sepiolite) were compared with the product distribution from the thermal decomposition of HDPE alone. The primary objective of this investigation was to evaluate the ability of clays and pillared clays (which have not been previously used for this purpose) to transform the thermally generated off-gases into useful products. Consequently, a detailed investigation of the material balance was outside the scope of this preliminary study. This study is also the first to use TG–OTM–GC–MS (in which the the evolved gases are collected on an organic trap module (OTM) and then desorbed onto the GC column before separation and subsequent identification by MS) to identify the wide variety of products produced.

Experimental

Materials

The polymer used throughout this study was high density polyethylene, HDPE (Aldrich). The pillared clay catalysts employed in this study were provided by Straton Hi-Tech under the Concerted European Action on Pillared Layered Solids.[15] Both pillared clays are produced from the same source mineral. AZA has pillars formed from aluminium oxyhydroxy cations whilst FAZA contains mixed Al,Fe pillars. K10 (Fluka), and acid-treated sepiolite (Tolsa SA, Spain) were used as received. The manufacturers' data for the surface area of AZA, FAZA and K10 are 225, 240 and 200 $m^2\ g^{-1}$. No comparable data are available for the acid-treated sepiolite. The thermal desorption of cyclohexylamine[24,25] was used to determine the acidity of the various samples yielding values of 0.2, 0.32, 0.34 and 0.43 mmol H^+ (g sample)$^{-1}$ for K10, FAZA, AZA and sepiolite, respectively.

Apparatus

Thermal and catalytic degradations of HDPE were carried out using a Synergic chemical analysis system supplied by Thermo Unicam. This system consists of a thermobalance (TG131, Cahn) fitted with two outlets which are connected to heated transfer lines. One transfer line was connected to an infrared gas cell (10 cm path length) contained in an infrared (FTIR) spectrometer (Infinity Series, Mattson). The outlet from the infrared gas cell flowed into a third transfer line which was connected to an absorbent trap (VOCARB 4000, Supelco) contained in an organic trap module (OTM, Cahn). The outlet from the OTM was also connected to a gas chromatograph-mass spectrometer (GC-MS) (Automass System 2, Unicam). The second transfer line was connected to the GC interface of the mass spectrometer. Preliminary experiments established that it was impossible to obtain pertinent information from TG–FTIR and TG–MS because of the complexity of the gas mixtures being evolved, consequently the data reported were obtained using TG–OTM–GC–MS.

Procedures

HDPE (50 mg) was placed in the TG sample crucible and 50 mg silanized glass wool was used to cover the polymer. Two separate heating regimes were utilised; the sample was heated from 25 °C to (i) 650 °C at 10 °C min^{-1} or (ii) 420 °C at a rate of 10 °C min^{-1} then held isothermally at 420 °C for 60 min. Dry nitrogen purge gas at atmospheric pressure (40 ml min^{-1}) was used in both regimes. Identical conditions were used during catalyst evaluation except that 200 mg catalyst was spread evenly over the glass wool so that gases evolved from the sample passed through the layer of catalyst. The results presented here do not contain information regarding the influence of the weight of catalyst used or the effect of diffusion through the catalyst bed. These operating temperatures were chosen since they represent the initial stages of and complete decomposition, respectively.

On completion of a TG run, the species contained on the trap were thermally desorbed (4 min at 250 °C) onto the GC capillary column (DB-1, 30 m × 0.25 mm id) where the compounds were separated before identification by MS. The transfer lines were maintained at 250 °C throughout the analyses. In a typical experiment the column was held at 35 °C during the 4 min desorption period before ramping the temperature at 5 °C min^{-1} to 250 °C. The final temperature was maintained for 5 min. To ensure that no decomposition products were left on the trap it was taken through the desorption cycle again to confirm that all the sorbed products had entered the GC. In addition, each trap was baked at 300 °C for 3 h and its cleanliness was confirmed by taking it through the desorption cycle before using it in subsequent analyses.

The relative amount of each species was determined by evaluating the area under the base peak for each aliphatic or aromatic species. This approach overcomes difficulties associated with co-eluting species. The results are reported as a percentage of the largest amount of product in a given comparative dataset.

Coke content

Upon completion of a catalytic process the system was cooled to 30 °C and the coked catalyst removed and stored. 50 mg of used catalyst was later placed in the TG sample crucible and heated from 25 to 650 °C at a rate of 10 °C min^{-1} under a flow of dry nitrogen (40 ml min^{-1}). At 650 °C the nitrogen was replaced with a flow of dry air (40 ml min^{-1}) and the sample held at 650 °C for 30 min to remove the deposited coke.

Results

TG data

The weight loss *vs.* temperature curve for the dynamic thermal decomposition of HDPE [Fig. 1(a)] shows that the decomposition was a one step process which began at 380 °C and finished at 470 °C, during which 98.53% of the initial weight of HDPE was lost. The chosen process temperatures were also convenient for catalyst activation since they were all substantially dehydrated by the onset temperature of polyethylene volatilisation. FTIR analysis (not shown) of the off gases produced in the temperature region 35–300 °C (Fig. 1) con-

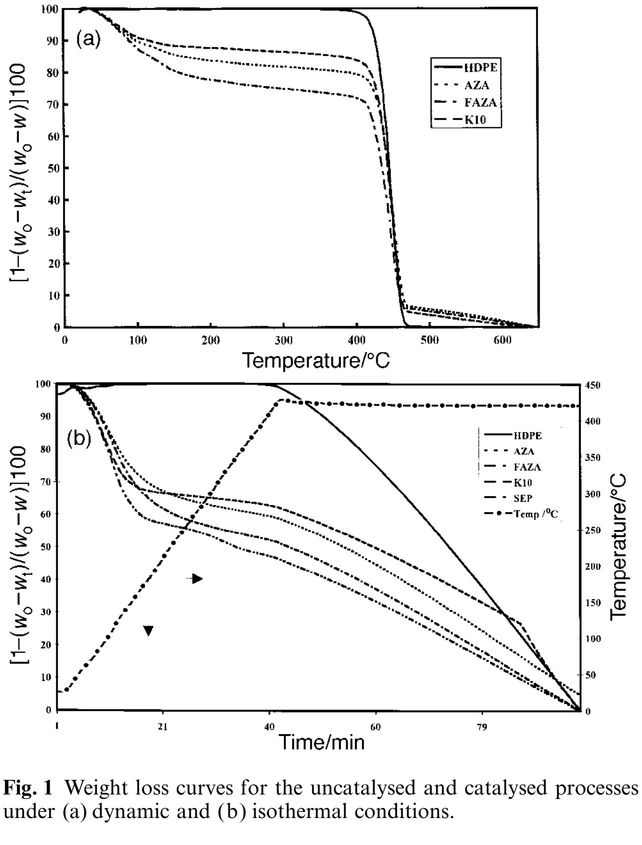

Fig. 1 Weight loss curves for the uncatalysed and catalysed processes under (a) dynamic and (b) isothermal conditions.

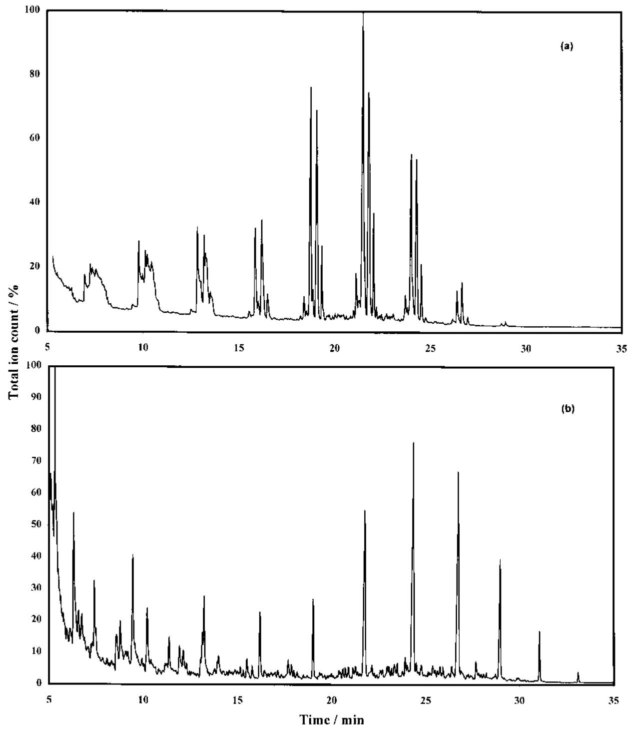

Fig. 2 GC–MS chromatogram of the products evolved during (a) the thermal decomposition of HDPE and (b) the K10 catalysed transformation of the product distribution shown in Fig. 2(a) under dynamic conditions.

firmed that only water was evolved. Fig. 1(b) shows that the rate of weight loss during the isothermal process was more gradual than under dynamic conditions which may mean that each volatile product took longer to pass through the catalyst bed.

TG–OTM–GC–MS

Fig. 2(a) shows the total ion chromatogram (TIC) *vs.* time curve obtained after HDPE was heated to 650 °C and a similar distribution was obtained in the isothermal process. The major products eluted as quartets of peaks, and the general character of the distribution is very similar to published data for the thermal degradation of HDPE.[2–5,10]

Mass spectrometric analysis of each individual peak showed that the product gases were a mixture of *n*-alkanes, alk-1-enes, alk-*x*-enes (alkene with internal double bond), α,ω-dienes and a range of branched aromatic and polyaromatic species. The individual compounds named were identified from their fragmentation patterns and parent ions. Alkanes exhibit a parent ion of mass $C_nH_{2n+2}^+$, alkenes exhibit parent ions of mass $C_nH_{2n}^+$ and dienes exhibit parent ions of mass $C_nH_{2n-2}^+$. Alk-1-enes and alk-*x*-enes were identified (and discriminated between) by the fragmentation patterns obtained for each compound. This collection of organic compounds was present in all the product mixtures but the quantity and distribution of the individual components was significantly affected by the process temperature and the transformation catalyst used. The four major components in the 'quartet' of peaks, in order of increasing retention time, were α,ω-diene, alk-1-ene, *n*-alkane and alk-*x*-ene.

Thermal degradation

The dynamic thermal decomposition of HDPE up to 650 °C yielded *n*-alkanes, alk-1-enes, alk-*x*-enes and α,ω-dienes in the range C_4–C_{20}. Species of higher molecular weight than C_{20} were not detected, and there was no evidence for branched alkanes in any region of the gas chromatogram. These observations are in accord with those of others.[4,10] There was evidence for branched alkenes at low molecular weights ($\leqslant C_7$) but no branched, unsaturated species of higher molecular weight were identified. The extremely low yield of aromatic species was anticipated.[4]

Fig. 2(b) shows that after passing the vapours evolved during dynamic thermal decomposition of HDPE through K10 there was little evidence of the alk-1-enes, alk-*x*-enes and α-ω-dienes. This dramatic transformation in the chromatogram occurred with all of the catalysts studied.

In order to simplify presentation the approach of Uddin *et al.*[3] has been adapted to illustrate changes in the distribution of linear products, *i.e.* the relative base peak area for each alkane was plotted against the number of carbon atoms in the chain. Comparison of the TICs in Fig. 2 with the distributions in Fig. 3 shows that (for the thermally decomposed products) the distribution refers to both alkanes and alkenes, whereas for the products obtained after contact with K10 and the other catalysts used [Fig. 2(b)] it only represents the alkane distribution. The distribution of saturated aliphatic hydrocarbons evolved during thermal decomposition of HDPE up to 420 °C agrees with the data of Uddin *et al.*[3]

GC–MS analysis of the thermal decomposition products identified small amounts of several aromatics, the most abundant of which at 650 °C was toluene, with lesser amounts of the xylenes. In addition, traces of ethylbenzene, ethylmethylbenzenes, naphthalene and substituted naphthalenes were found at both process temperatures (Fig. 4 and 5).

Catalytic transformation of evolved gases

In general the action of the catalysts on the gases evolved during the dynamic decomposition of HDPE resulted in a distribution of *n*-alkanes in the range C_4–C_{20} (which maximised at C_{13}–C_{16}), with branched alkanes up to C_{20}. There was a complete absence of polyunsaturated species, and the alkenes (both branched and linear) were confined to $<C_7$ as observed for the decomposition of HDPE over silica-alumina.[5] The distribution of alkanes obtained over K10 and sepiolite moved to higher carbon numbers whereas that for AZA moved downwards. At 420 °C the alkane distribution over all catalysts was broadened and shifted to lower carbon number.

The data presented in Fig. 4 and 5 clearly show that all the catalysts produced considerably more aromatics than thermal decomposition at the same temperature, although the yield of polyaromatic species was never very large except when using FAZA. AZA produced the largest quantity of aromatic molecules at 650 °C (Fig. 5) and was very selective to xylenes although the distribution was shifted towards tri- and tetramethylbenzenes at 420 °C. FAZA produced the highest aromatic yield at 420 °C, was not as selective as AZA and produced significant quantities of naphthalene and its methyl substituted counterparts. K10 produced respectable quantities of methylbenzenes under isothermal and dynamic conditions, whilst sepiolite was more effective at 420 °C (Fig. 4 and 5). The extent of dealkylation on solid acid catalysts generally depends upon the relative ease of formation of alkyl carbonium ions,[26] and given that methylcarbonium ions are very difficult to form, most of the aromatics produced would not undergo further decomposition. These considerations are supported insofar as the range of the aromatic species produced changed very little with process temperature.

The coke values (Table 1) show that AZA, and particularly FAZA, coked up appreciably. The high iron content in FAZA probably accounts for the greater coke production, yet it is still considerably less than that found in catalyst/HDPE mixtures *viz.* 7% with zeolite US-Y,[27] 6 (±0.5)% over silica-alumina[28] and up to 19% on Ca-exchanged zeolite-X.[6]

As aromatics are adsorbed more strongly on acid catalysts than saturated hydrocarbons, it seems reasonable to assume that aromatics, particularly those with condensed rings such

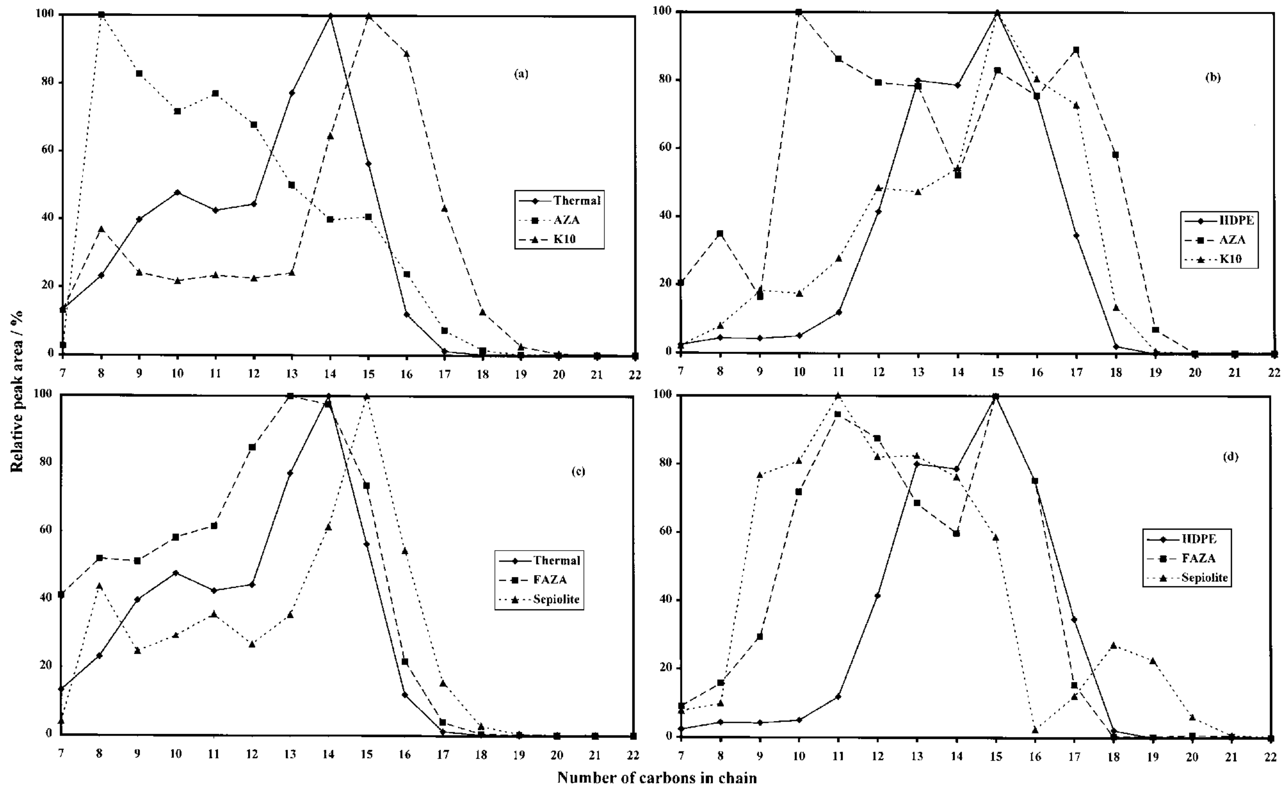

Fig. 3 Comparison of the distribution of carbon chain lengths (derived from GC–MS chromatograms) obtained under dynamic and isothermal conditions for AZA and K10 [(a) and (b), respectively] and FAZA and sepiolite [(c) and (d), respectively]. The distribution of the thermally derived products is shown in each of (a), (b), (c) and (d) for direct comparison.

as naphthalenes, most closely relate to coke deposition.[6] Uemichi *et al.* reported a 95% reduction in surface area when the pores in CaX were severely congested with a 19% coke deposition during the catalytic degradation of polypropylene.[6] This resulted in significant diffusional barriers to the ingress of the polypropylene decomposition products and hence their catalytic reformation was reduced.

Discussion

It is well known that the thermal degradation of polyethylene begins with a reduction in molecular weight near 290 °C, that the rate of degradation to volatile products increases with temperature and that the rate of chain scission is not a random process. Chain cleavage occurs *via* β-scission and one double bond appears for each cleavage event giving rise to alk-1-enes, alk-*x*-enes and α,ω-dienes. The small quantities of aromatic products are probably caused by thermally induced dehydrocyclisation.

The evolution of volatile species from HDPE begins near 350 °C. At this temperature the majority of the interlayer galleries within K10 will be collapsed and only the external pores produced by acid leaching of the octahedral sheet will be available to the thermally degraded products of HDPE. A similar situation would pertain in the sepiolite sample since the structure will have folded thus reducing the size of the channels, but the pores produced by acid treatment will be accessible. By contrast the entire pore network of the pillared clays will be available since it is known to be stable at high temperatures. However, the pore networks in AZA and FAZA are not identical and the different pillar compositions are likely to influence both the product distribution and the amount of coke formed.

The shift in the alkane product distribution to higher carbon numbers (Fig. 3), when the evolved gases were passed over K10 (at both 420 and 650 °C), was attributed to catalytic alkylation on the open porous surface of the acid-activated clay although termination *via* recombination may also be occurring. More striking than the upward shift of carbon number over the acid-activated clays was the very significant increase in the lower molecular weight compounds produced by the pillared clays, particularly AZA at 650 °C. A similar observation was reported for the decomposition of polyethylene in the presence of rare-earth exchanged zeolite-Y.[10] The data presented in Fig. 4 and 5 clearly show that a considerable portion of these low molecular weight species are methylaromatics and that AZA is the most active in their production. This shift towards lower molecular weight and/or aromatic species is attributed to β-scission and dehydrocyclisation, respectively.[13] In general, the catalysts decreased in their ability to produce aromatics as FAZA > AZA > K10 > sepiolite at 420 °C and AZA > FAZA > K10 > sepiolite at 650 °C.

Clearly, the pillared clays produced the most aromatics and no single ring molecules larger than ethylbenzene were identified which may be partly attributed to the relative stability of the methylaromatics.[6] This agrees with Uemichi's work using silica-alumina[5] but contrasts with studies involving the zeolite ZSM-5[13,29] where benzene was identified even though it was less abundant than toluene and the xylenes. Unfortunately, whilst benzene was identified in the current investigation, quantification was unrealistic because it co-eluted with several low boiling species. Indeed, catalytic degradation over ZSM-5 favours formation of large quantities of low molecular weight gases (C_3–C_4) because the small pore opening in this zeolite prevents molecules with more than three or four carbon atoms from entering the channel network—a feature which is put to excellent use in the dewaxing process.[30] Nonetheless, ZSM-5 is able to produce aromatics as a secondary product when molecules, pre-cracked on the external surfaces, enter the channel network.[7] Ohkita *et al.*,[29] in a more extensive study than that of Uddin *et al.*,[3] correlated the acidity of silica-aluminas, of selected composition, with the products formed when thermally degraded polyethylene was passed over the catalysts and found that as the surface acidity

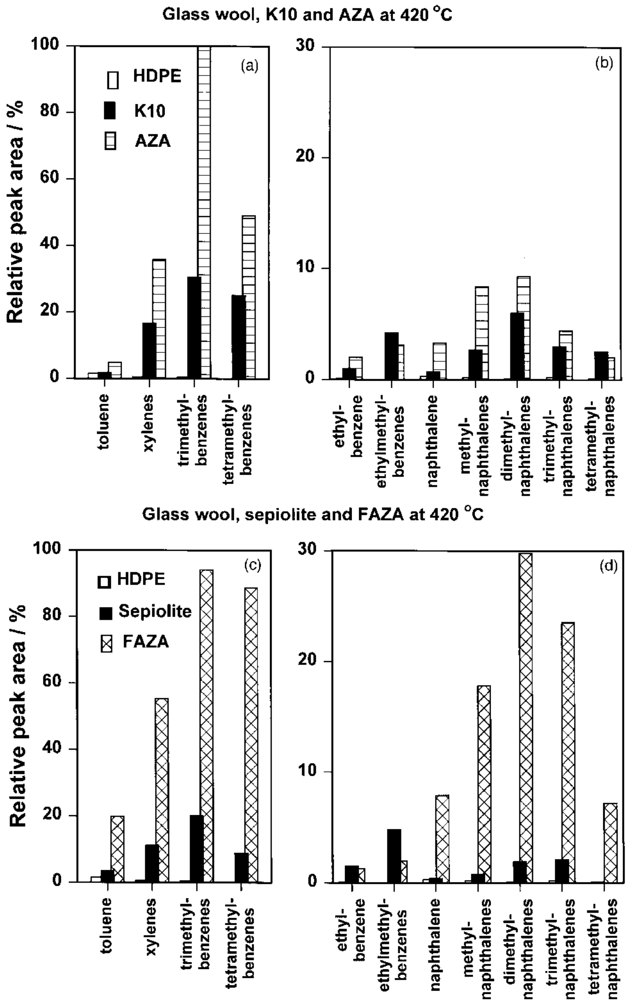

Fig. 4 Distribution of unsaturated products from the catalysed transformation of thermally evolved products over AZA and K10 under isothermal conditions. (a), (b) HDPE, K10 and AZA; (c), (d) HDPE, sepiolite and FAZA.

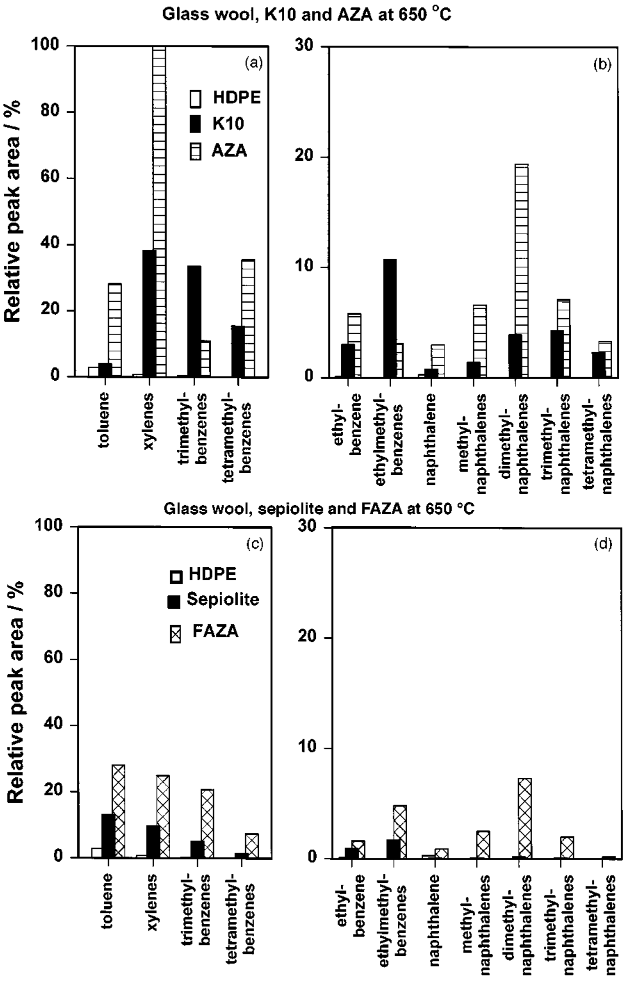

Fig. 5 Distribution of unsaturated products from the catalysed transformation of thermally evolved products under dynamic conditions. (a), (b) HDPE, K10 and AZA; (c), (d) HDPE, sepiolite and FAZA.

Table 1 Coke values for acid-activated and pillared clays

Catalyst	Coke content for isothermal process (wt%)	Coke content for dynamic process (wt%)
AZA	2.0	1.3
FAZA	4.0	2.4
K10	0.9	0.7
Sepiolite	0.9	0.1

increased the proportion of the gaseous fraction increased whilst that of the oil fraction decreased. They also reported that ZSM-5 produced three times more aromatic products and three times less paraffinic species than the most active silica alumina. However, not all zeolites are as active as ZSM-5. Herein sepiolite contained the highest number of acid sites thus it is possible that the lack of aromatic species produced was due to the major product being light gases which were not detected.

Songip *et al.*[31,32] showed that the acid form of ZSM-5 was not suitable for the reforming of heavy oil derived from polyethylene. Unfortunately, even though it produced gasoline with a good octane number and did not readily coke up, the yield (20%) was much lower than the amount of gas produced (68%). In comparison proton-exchanged (HY) and rare earth-exchanged (REY) zeolite-Y produced gasoline of comparable quality in higher yield with up to 30% less gas. HY contains a larger number of more acidic sites than REY resulting in a lower gasoline yield (27% *vs.* 49%) and a faster deactivation rate thus producing larger amounts of both gas (44 *vs.* 35%) and coke (6 *vs.* 3%). REY was the optimum choice since its larger pore size permitted ingress of the heavy oil and it had fewer acid sites which resulted in a reduced deactivation rate and less coke deposition.[31,32]

The behaviour of the catalysts used here mimics that of the REY samples since PILCs and acid-activated clays are known to have a larger number of milder acid sites than most zeolites[16] and pillared clays have predominantly Lewis acid sites after activation at high temperatures.[33–36] Consequently, the large, unsaturated molecules produced during the thermal degradation of HDPE were cracked into smaller molecules and aromatics were produced *via* dehydrocyclisation but there was no overcracking to the small gaseous molecules which occurred over the large number of strong acid sites in the microporous ZSM-5. Utilising the same experimental procedure as those used here ZSM-5 cracked both the saturated and unsaturated hydrocarbons into low molecular weight gases. Consequently, the characteristic distribution profile, such as that shown for the products from K10 in Fig. 2(a), was not observed and less aromatic species were produced (unpublished results).

Fig. 4 and 5 show that there was a major shift in the products formed over AZA from tri- and tetra-methylbenzene, in the isothermal process, to xylenes in the dynamic process. This probably reflects a combination of factors including the lower feed rates to the catalysts in the isothermal process which would favour the formation of the more substituted products.[6] In contrast the distribution of alkylated benzenes produced over K10 did not change as much, except for a significant reduction in the ethylmethylbenzenes.

Although the coke values on sepiolite were equal to or lower than that on the other catalysts (Table 1) and the overall weight change was very similar to that in the presence of the other catalysts the production of aromatic products was comparatively low in both processes. However, significant quantities of branched and straight unsaturated molecules of $\leqslant C_7$ were produced in both the dynamic and isothermal processes, suggesting that there were sites on the sepiolite which were able to dehydrogenate and crack the thermally decomposed products but that only a small number of dehydrocyclisation sites were present. It is also possible that a major product, *e.g.* low molecular weight gases and/or benzene, was not readily identified using the procedure herein. Consequently, although there is no direct evidence to support the interpretation it is possible that the lack of aromatic production over sepiolite at 420 °C derives, in part, from the formation of low molecular weight gases in the microporous channels of the sepiolite. When the channels have completely collapsed upon heating to higher temperatures the distribution of aromatic products closely resembles that of the acid-treated bentonite, K10.

The high aromatic production over AZA and FAZA suggests that the dehydrocyclisation sites may be associated with the pillars. However, edge sites on the clay layers may also play a significant role because these would be altered in the acid treatment of K10 and sepiolite but would remain unchanged by the pillaring process. However, the current data do not permit an unequivocable differentiation between the two possibilities.

Conclusions

The thermal decomposition of HDPE up to 650 °C yielded characteristic quartets of peaks assigned to *n*-alkanes, alk-1-enes, alk-*x*-enes and α,ω-dienes in the range C_4–C_{22}. Species of higher molecular weight than C_{22} were not detected. All four catalysts converted the alkenes present in the thermally generated off gases into light gases and aromatic species including respectable quantities of toluene, xylenes, tri- and tetra-methylbenzenes. Ethylbenzenes and naphthalenes were produced to a lesser extent. None of the catalysts used was capable of cracking the saturated alkanes and so no overcracking took place. The aluminium pillared clay produced the largest yield of aromatics and sepiolite is considered to produce significant quantities of low molecular weight gases in the isothermal process.

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Paper 8/08882I