

## Synergic chemical analysis — the coupling of TG with FTIR, MS and GC-MS

### 2. Catalytic transformation of the gases evolved during the thermal decomposition of HDPE using acid-activated clays

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#### Abstract

High-density polyethylene, HDPE, has been thermally decomposed in a thermobalance and the evolved gases passed through a bed of catalyst. The resulting transformation products were trapped and subsequently identified using GC-MS. Two smectites of different octahedral compositions were acid-activated under conditions known to produce catalysts of differing activity. Three different treatments were used for each smectite, thus providing six samples for evaluation. The thermal and catalytic decomposition of HDPE was studied under isothermal (60 min at 420°C) and dynamic (35–650°C at 10°C min<sup>-1</sup>) conditions. The thermal decomposition of HDPE yielded characteristic quartets of peaks in the chromatogram which were assigned to *n*-alkanes, 1-alkenes, *x*-alkenes and  $\alpha,\omega$ -dienes in the range C<sub>4</sub>–C<sub>22</sub>. Species of higher molecular weight than C<sub>22</sub> were not detected. All six catalysts converted the alkenes present in the thermally generated off gases into light gases and aromatic species. Mono-, di- and trimethylbenzenes were the most abundant aromatic species although small quantities of ethylbenzenes and naphthalenes were produced. More aromatics were produced at 420°C than at temperatures up to 650°C, whereas the reverse was true for branched alkanes. The total conversion of HDPE increased with both the extent of acid treatment and the process temperature, whereas the proportion of aromatics produced was greatest for catalysts prepared using short acid-treatment times. © 2000 Elsevier Science B.V. All rights reserved.

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#### 1. Introduction

The low weight-to-volume ratio and the time that waste polymers take to degrade means that land filling is not an acceptable option [1]. Nor is incineration,

because this leads to a variety of products any one of which could present an environmental hazard when released into the atmosphere. Moreover, the chemical content of the polymer is lost when either of these two options are used [2]. Consequently, as the amount of waste polymers continues to increase, investigations into the potential recycling of polymers and the successful reclamation of their chemical content are of increasing importance. Thermal pyrolysis has been studied as a means of recovering high-value products from the gases evolved during polymer degradation

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[3,4]. The products recovered from polyethylene are, in the main, alkenes and saturated hydrocarbons in the range  $C_2$ – $C_{25}$  of a broad distribution [3] with average chain lengths of 13.2 to 14.5 [4]. British Petroleum have established a fluidised bed reactor system but it is not considered to be a profitable process. Significant conversion to relatively high-value aromatic products is seldom achieved.

Catalytic degradation of polymers offers the potential benefits of lower operating temperatures [3] and an increase in the rate of polymer decomposition [1] together with the generation of high-value chemicals [3] in a product mixture which contains fewer components [5]. Two distinct methods have been employed when catalysts are used: (1) mixing the catalyst and polymer together thus ensuring close physical contact between the two [1–9], (2) directing the thermal decomposition products derived from the polymers over a catalyst which is physically distant from the polymer [10–13]. Most catalytic investigations have been conducted under nitrogen, but investigations involving hydrogen [2,8] and high pressures [8] have recently been reported. Both the nature and the distributions of species, evolved during pyrolysis [3,5], are changed when catalyst and polymer are present in a mixture. In the presence of a silica–alumina catalyst, Uemichi et al. [6] reported the presence of *n*-alkanes, iso-alkanes, alkenes and aromatics whilst Uddin et al. [3] observed a narrower distribution of hydrocarbons (*n*- $C_2$  to *n*- $C_{15}$ ). In the former case the distribution of alkanes (6% yield) focussed in a narrow range ( $C_3$ – $C_5$ ) but isoalkanes and alkenes (35 and 44%, respectively) were more prominent than aromatics (11%).

Numerous catalysts have been evaluated for the pyrolytic decomposition of polymers, notably zeolites [2,6,7,9–12] and silica–alumina mixed oxides [3,5,6,9,10,13]. In contrast, acid-activated clays have received scant attention even though they represent a convenient, cheap and widely available alternative to expensive manufactured catalysts. A significant challenge to the use of clays as catalysts is that their potentially extensive surface area becomes unavailable at temperatures  $> 150$ – $200^\circ\text{C}$ , because the molecules occupying the clay galleries are desorbed and the layers come into direct contact forming a collapsed clay. Acid leaching of the clay was found to increase both the surface area and the available

acidity sufficiently for them to be used as cracking catalysts in the petroleum industry [14]. During acid-activation of clays the ions in the octahedral sheet are leached out, the nitrogen surface area increases, the number (and type) of acid sites changes as do the sorptive and catalytic properties. These properties generally maximise under intermediate activation conditions and, subsequently, decrease as the product takes on the properties of amorphous silica, which has been identified as the final product of acid leaching [15–18]. It is now widely accepted that clays with a high octahedral Mg content leach more readily than those which have a high octahedral Al population [18–24] and recent reports have established that clays with a high octahedral Fe content also leach rapidly [25–27]. An extensive investigation into the acid-leaching of a range of smectites (selected for their differing octahedral ion content) has shown that the elemental composition of the starting material does not make a significant contribution to the catalytic activity for the chosen test reaction, but is the critical factor when determining the severity of the activation conditions required for the optimisation of the catalyst [27]. Both the clays used herein are the fine fractions of Slovak bentonites: Jelsovy Potok, JP, and Stebno, ST. The acid-activation of these two clays [27], and their organocation exchanged counterparts, has recently been described [28].

It has recently been established that pillared and acid-activated clays have the ability to transform the thermal decomposition products of high-density polyethylene (HDPE) into useful products, although only one example of an acid-treated smectite was investigated [29]. In the present study, the distributions of the secondary cracking products obtained when the thermal degradation products from HDPE (which along with PET has been identified as a significant target for catalytic conversion into useful products [30]) are passed over the acid-activated smectites and compared with the product distribution from the thermal decomposition of HDPE alone. The primary objective of this investigation was to ascertain how the nature of the starting clays and the extent to which they were acid leached influenced their ability to transform the thermally generated off-gases into useful products. Consequently, a detailed investigation of the material balance was not a primary focus. Use of TG-OTM-GC-MS (*vide infra*) permits the identification of the

products of either thermal decomposition or secondary cracking from each catalyst and comparison of the relative abundances of the products.

## 2. Experimental

### 2.1. Materials

The polymer used throughout this study was high-density polyethylene, HDPE, (Aldrich). JP is a hydrothermal, aluminium rich, dioctahedral montmorillonite from the Kremnica Mountains in central Slovakia [31,32]. In contrast, the main mineral in Stebno, ST, from the Czech Republic is Fe-beidellite which has an octahedral sheet rich in iron and 57% of the charge on the layer arises from substitution in the tetrahedral sheet. ST contains about 21% of total iron bound in goethite [33] which is present as an admixture in the  $< 2 \mu\text{m}$  fraction and, hence, could not be removed by fractionation. However, it is readily dissolved in 6 M HCl, thus the acid-activated samples contain no goethite. Coarse samples of JP and ST were suspended in deionised water, treated five times with 1.0 M aqueous calcium chloride, washed until free of chloride, centrifuged, and the nominally  $< 2 \mu\text{m}$  sample was collected, dried at  $60^\circ\text{C}$  and ground to  $< 0.2 \text{ mm}$  prior to storage. The structural formulae of the purified smectites used are given in Table 1.

### 2.2. Equipment and methods

Three-gram portions of the Ca-form of each mineral were treated with  $300 \text{ cm}^3$  of 6 M HCl for different periods of time. JP and ST were treated at  $95^\circ\text{C}$  and  $60^\circ\text{C}$ , respectively, since it has been shown that ST is

Table 1  
Structural formulae of smectites in the fine fractions of the samples used

Sample	M <sup>+</sup> <sup>a</sup>	Si <sup>b</sup>	Al <sup>b</sup>	Al <sup>c</sup>	Fe <sup>c</sup>	Mg <sup>c</sup>	Li <sup>c</sup>
JP <sup>d</sup>	0.91	7.71	0.29	3.00	0.38	0.63	0.00
ST <sup>e</sup>	0.95	7.22	0.78	1.96	1.60	0.58	0.00

<sup>a</sup> Interlayer cations.

<sup>b</sup> Tetrahedral cations.

<sup>c</sup> Octahedral cations.

<sup>d</sup> Ref. [19].

<sup>e</sup> Ref. [27].

leached more readily than JP [27]. After acid treatment the samples were filtered, then washed with  $1.5 \text{ dm}^3$  deionised water and centrifuged before being dried and ground to pass a 0.2-mm sieve. The treatment time is identified in the sample name. Thus, JP30 indicates that JP was treated in 6 M HCl for 30 min at  $95^\circ\text{C}$ , and ST120 means that ST was treated with 6 M HCl for 120 min at  $60^\circ\text{C}$ . The characterisation of these materials has been described elsewhere [27].

### 2.3. Apparatus

Thermal and catalytic degradations of HDPE were carried out using a synergic chemical analysis system supplied by Thermo Unicam [34]. 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 second 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 third transfer line was connected directly to the mass spectrometer (Automass System 2, Unicam). 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.

### 2.4. Procedures

HDPE (50 mg) was placed in the TGA sample crucible and glass wool (50 mg) was placed on the HDPE to cover the polymer. Two separate heating regimes were utilised; the sample was heated from  $25^\circ\text{C}$  to (i)  $650^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$  or (ii)  $420^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ , then held isothermally at  $420^\circ\text{C}$  for 60 min. Dry nitrogen purge gas at atmospheric pressure ( $40 \text{ ml min}^{-1}$ ) was used in both regimes. Identical conditions were used during catalyst evaluation, except that 200 mg of acid activated clay was spread evenly over the glass wool so that gases evolved from the sample passed through the layer of catalyst [29]. 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 the TG analysis, 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 I.D.) 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<sup>-1</sup> to 250°C. The final temperature was maintained for five minutes. Considerable care was exercised to ensure that no sample was left on the traps after the desorption cycle. The traps were taken through the desorption cycle again in order to confirm that all the sorbed products had entered the GC. In addition, each trap was baked at 300°C for three hours and its cleanliness was confirmed by taking it through the desorption cycle prior to collecting the evolved gases.

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.

### 2.5. Coke content

After a typical run, the system was cooled from its maximum temperature to 30°C so the coked catalyst

could be removed and stored. Fifty milligrams 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<sup>-1</sup> under a flow of dry nitrogen (40 ml min<sup>-1</sup>). At 650°C, the flow of nitrogen was replaced with a flow of dry air (40 ml min<sup>-1</sup>) at atmospheric pressure and held at 650°C for 30 min to oxidise deposited coke on the catalyst. The coke content was calculated from the weight loss.

## 3. Results

### 3.1. Catalyst properties

Table 2 presents data for the depopulation of the clay layer, the acidity determined using the desorption of cyclohexylamine and the yield obtained using these catalysts in a liquid phase test reaction [27]. This data shows that ST was more readily leached under milder conditions than JP and this is attributed to the different octahedral compositions (Table 1). ST is rich in iron whereas JP contains more aluminium.

### 3.2. TG data

The weight loss versus temperature curve for the thermal decomposition of HDPE under a linear heating rate (Fig. 1a) shows that the decomposition was a single step process with offset and end temperatures of 380°C and 470°C, respectively, during which 98.53% of the initial weight of HDPE was lost. The temperatures chosen were also convenient for catalyst activation since they were all substantially dehydrated by the

Table 2  
Relevant data for catalyst composition acidity coke content and catalytic ability

Catalyst	Octahedral sheet depletion <sup>a</sup> /%	Acidity <sup>a</sup> (mmol H <sup>+</sup> g clay <sup>-1</sup> )	Yield in ether forming reaction <sup>a</sup> (%)	Amount of HDPE converted at 420°C <sup>b</sup> (%)	Coke content for isothermal process (wt.%)	Coke content for dynamic process (wt.%)
ST30	14	1.05	83	52	1.0	0.6
ST120	29	0.97	71	76	1.0	0.4
ST240	45	0.80	68	95	0.9	0.4
JP120	11	1.00	97	70	2.0	0.9
JP240	22	0.96	92	80	1.7	0.8
JP360	39	0.70	68	98	1.5	0.6

<sup>a</sup> Ref. [27].

<sup>b</sup> The conversion of HDPE at 650°C was virtually 100%.

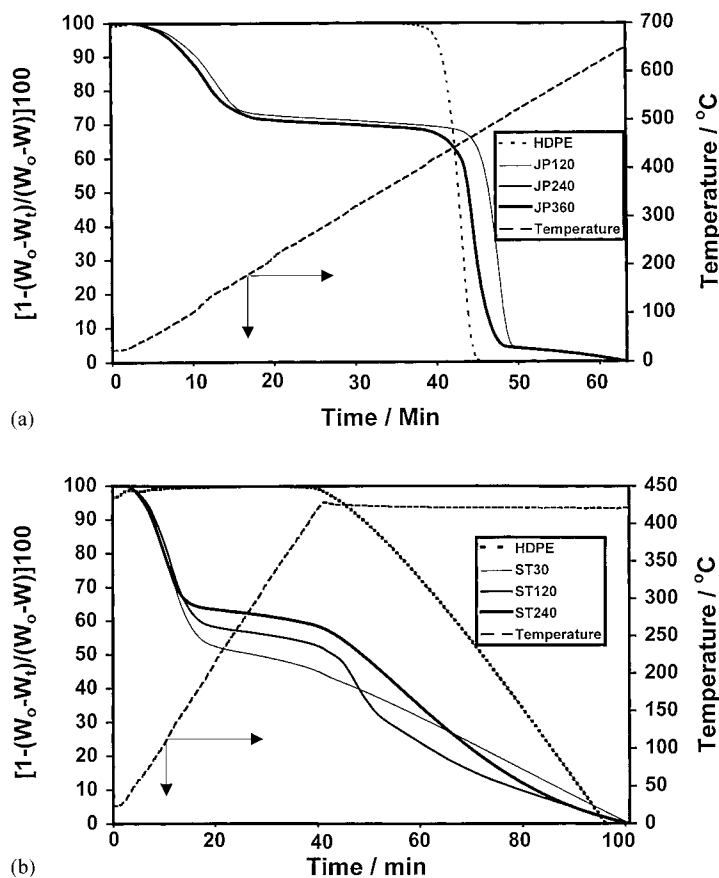


Fig. 1. Weight loss curves for the uncatalysed and catalysed processes under (a) dynamic, and (b) isothermal conditions. The curves for JP240 and JP360 overlap in 1(a) and are not distinguishable.

onset temperature of polyethylene volatilisation. FTIR analysis (not shown) of the off gases produced in the temperature region 35–300°C (Fig. 1) confirmed that only water was evolved. It is well known that clays are effectively dehydrated by 300°C and the layers would have collapsed leaving only the pores created by acid-activation available for the catalytic process. Incidentally, no hydroxylated compounds could be found in the product stream confirming that there was little or no interlayer water remaining on the catalyst surface to react with the alkenes. Fig. 1, in which the weight losses are normalised, shows that there were noticeable differences in the rate of weight loss during the isothermal process (Fig. 1b) and that the weight losses occurred more gradually at 420°C than at 650°C. This means that the rate at which HDPE was delivered to the catalyst at 420°C was much slower than at 650°C.

In addition, whilst all the HDPE was thermally degraded at 650°C, up to 50% remained at 420°C depending on the extent of acid treatment of the catalyst (Table 2). The catalysts with the more extensive octahedral depopulation caused the most extensive reduction in the amount of HDPE remaining.

### 3.3. Thermal degradation

Fig. 2a shows the total ion chromatogram (TIC) versus time curve obtained when HDPE was heated at 420°C. A similar distribution was obtained under dynamic conditions. The general character of the distributions is very similar to published data for the thermal degradation of HDPE [2–5,10] and shows that the major products eluted as quartets of peaks. Mass spectrometric analysis of each individual peak

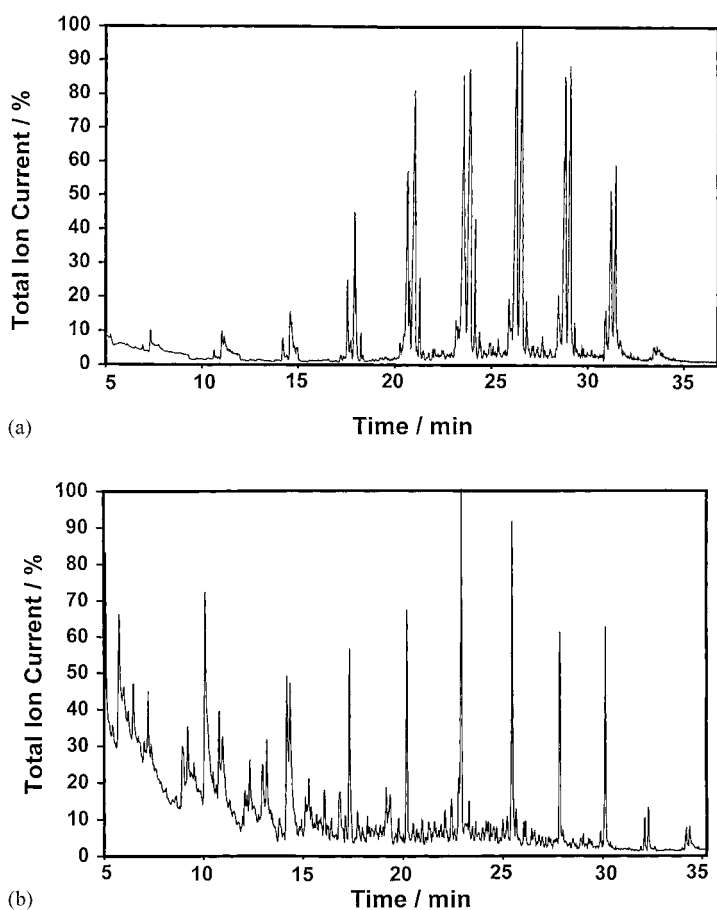


Fig. 2. GC-MS chromatogram of the products evolved during (a) the thermal decomposition of HDPE and (b) the ST-30 catalysed transformation of the product distribution shown in Fig. 2a under isothermal conditions.

showed that the product gases were a mixture of *n*-alkanes, *I*-alkenes, *x*-alkenes (alkene with internal double bond),  $\alpha,\omega$ -dienes and a range of branched aromatic and polyaromatic species. In order of increasing retention time, the four major components in the 'quartet' of peaks were  $\alpha,\omega$ -diene, *I*-alkene, *n*-alkane and *x*-alkene. All these organic compounds were present in all the product mixtures, but the reaction temperature and the catalyst used significantly influenced the amount of each product. Each named compound was identified from its fragmentation pattern and parent ion. 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  $C_nH_{2n+2}^+$ . *I*-Alkenes and *x*-alkenes were identified (and discriminated between) by the fragmentation

patterns obtained for each compound. Fig. 2b shows that only one of the quartet of peaks remained after passing the vapours evolved during dynamic thermal decomposition through ST30. These peaks were those of the *n*-alkanes and there was little evidence of the *I*-alkenes, *x*-alkenes and *x*-dienes. This dramatic transformation in the chromatogram occurred with all of the catalysts studied.

The thermal decomposition of HDPE up to 650°C also yielded *n*-alkanes, *I*-alkenes, *x*-alkenes and  $\alpha,\omega$ -dienes in the range  $C_4$ – $C_{22}$ . Molecules longer than  $C_{22}$  were not detected, and there was no evidence for branched alkanes. There was evidence for branched alkenes at low molecular weights ( $\leq C_7$ ) but no branched, unsaturated species of higher molecular weight were identified. These observations are in

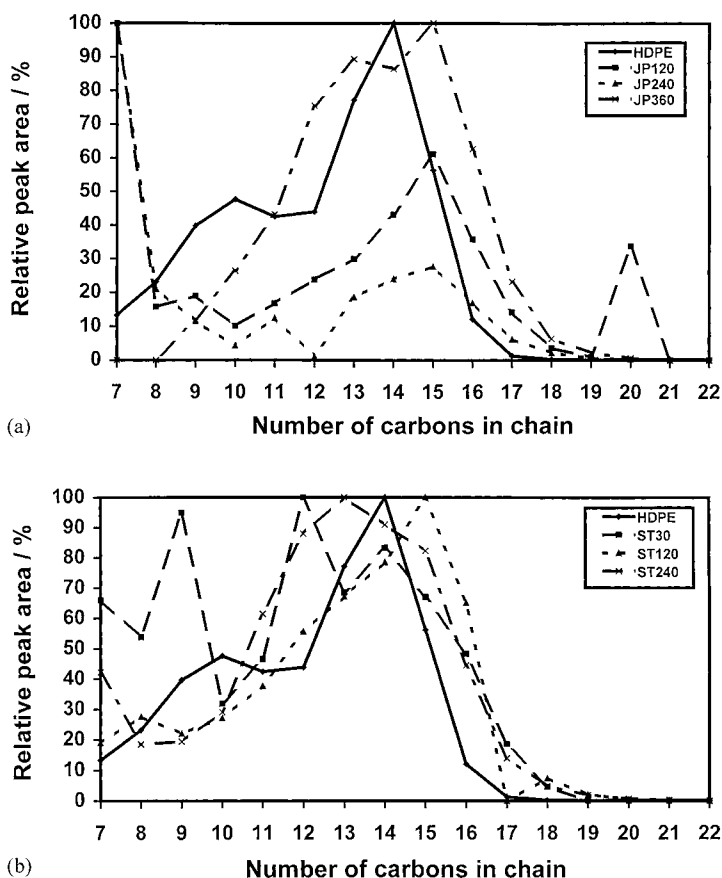


Fig. 3. Comparison of the distribution of carbon chain lengths (derived from GC-MS chromatograms) obtained under isothermal conditions for (a) JP and (b) ST. The distribution of the thermally derived products is shown in both (a) and (b) for direct comparison.

accord with those of others [5,10]. The extremely low yield of aromatic species was anticipated [5].

The approach of Uddin et al. [3] has been used to present changes in the distribution of linear products, i.e. the relative base peak area of the 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 the distribution refers to both the alkanes and alkenes (for the thermally decomposed products), whereas for the products obtained after contact with the catalysts (Fig. 2b) only the alkane distribution is reflected. The distribution of saturated aliphatic hydrocarbons evolved during thermal decomposition of HDPE at 420°C is similar to that found by others [3,29].

Small quantities of several aromatics were identified at both process temperatures (Figs. 4 and 5) using

GC-MS. The most abundant of these was toluene with lesser amounts of the xylenes along with traces of ethylbenzene, ethylmethylbenzenes naphthalene and substituted naphthalenes.

### 3.4. Catalytic transformation of evolved gases

The action of the catalysts on the thermally generated decomposition gases of HDPE generally produced a distribution of n-alkanes in the range C<sub>4</sub>–C<sub>22</sub> (which maximised at C<sub>11</sub>–C<sub>18</sub>), with branched alkanes up to C<sub>20</sub>. Indeed many more branched alkanes were produced at 650°C than at 420°C with ST30 producing the most. There was a complete absence of polyunsaturated species, and the mono-unsaturated species (both branched and linear) were confined to < C<sub>7</sub> as observed for the decomposition of

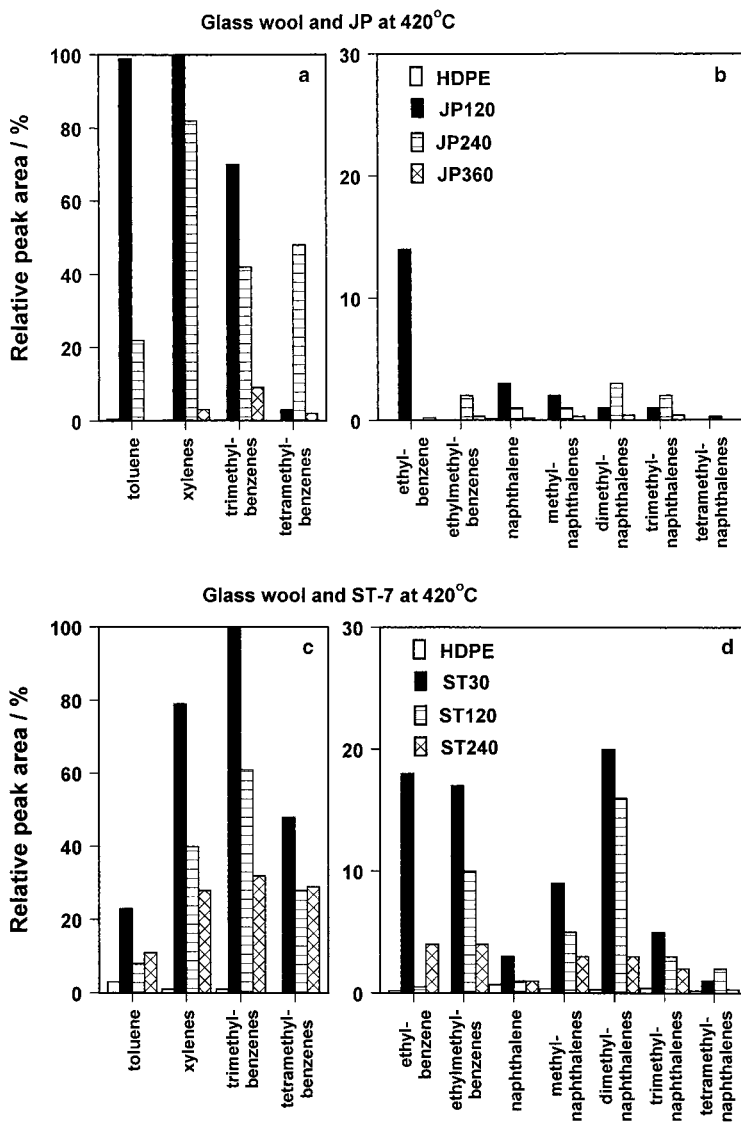


Fig. 4. Distribution of unsaturated products from the catalysed transformation of thermally evolved products over ST and JP under isothermal conditions. (a) and (b) HDPE and JP; and (c) and (d) HDPE ST.

HDPE over silica–alumina [4] and a selection of acid-treated and pillared clays [29]. The distribution of alkanes obtained over both sets of catalysts was broader at 420°C than at 650°C.

All the catalysts produced more aromatics than thermal decomposition at the same temperature (Figs. 4 and 5). The yield of polyaromatic products, which never exceeded 30% of the most abundant single ring compounds, was higher at 650°C. In gen-

eral, the aromatic production was lower at 650°C than at 420°C and decreased with the extent of acid treatment of the catalyst with JP120 at 420°C producing the most aromatic species. In contrast, the production of branched species was much higher at 650°C, but was also dependent on the level of acid treatment. The production of aromatics over JP360 at 420°C was lower than anticipated, given that it converted the most HDPE and was also an effective catalyst for



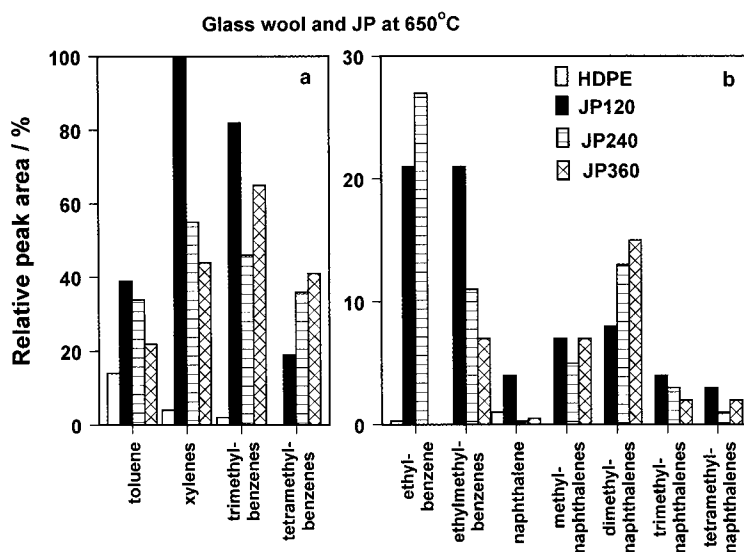


Fig. 5. Distribution of unsaturated products from the catalysed transformation of thermally evolved products over JP under dynamic conditions.

the formation of tetrahydropyran from dihydropyran and methanol [27]. However, it is important to realise that the formation of tetrahydropyran ether occurs under very mild conditions in the presence of liquid reactant, whereas the transformation of HDPE occurs at high temperatures when the clay is substantially dehydrated and not expanded.

Earlier work on the transformation of HDPE to useful products showed that aluminium pillared clays were selective to trimethylbenzenes at 420°C and xylenes at 650°C. The acid-treated clays used herein produce a wider range of single ring products similar to that reported for the transformation over K10, a commercial acid-treated material, of unspecified extent of leaching [29]. The extent of dealkylation on solid acid catalysts generally depends on the relative ease of formation of alkyl carbonium ions [35]. Since methylcarbonium ions are very difficult to form, most of the aromatics produced would be unlikely to undergo decomposition. These considerations are supported herein insofar as the composition of the aromatics changed relatively little with process temperature.

The coke values collected in Table 2 show that, despite the relatively high iron content in the catalysts derived from ST, they generally produced less coke than those derived from JP. Nonetheless, these values

are considerably lower than the 7% reported for the zeolite US-Y [36], 6% over silica–alumina [37] and up to 19% on Ca-exchanged zeolite-X [6] when the catalyst was ground together with the polymer. Given that aromatics are adsorbed more strongly on acid catalysts than saturated hydrocarbons it is assumed that aromatics, particularly the naphthalenes, most closely relate to coke deposition [6]. A 95% reduction in surface area occurred when the pores in CaX were severely congested with a 19% coke deposition during the catalytic degradation of polypropylene [6]. This severely restricted the inward diffusion of the polypropylene decomposition products and hence their catalytic reformation.

#### 4. Discussion

The thermal degradation of polyethylene begins with a reduction in molecular weight near 290°C and the rate of degradation to volatile products becomes more rapid as the temperature increases. Chain cleavage, which occurs via  $\beta$ -scission, produces one double bond per cleavage event giving rise to the 1-alkenes, *x*-alkenes and  $\alpha,\omega$ -dienes mentioned above. The small quantities of aromatic products are probably caused by thermally induced dehydrocyclisation.

The evolution of volatile species from HDPE begins near 350°C (Fig. 1), a temperature at which all the interlayer galleries in each of the catalysts will be completely collapsed and only the external pores produced by acid leaching of the clay layer will be available to the thermal degradation products of HDPE. Moreover, only those acid sites on the external surface and within the pores will be accessible, since it is unrealistic to assume that the non-polar alkenes will penetrate into the clay galleries at these elevated temperatures and re-expand the collapsed layers.

The situation at the catalyst surface is very complex involving protonation, isomerisation, alkylation, dehydrogenation/rehydrogenation coupled with the separate influences of temperature and residence time. All of these combine to make a clear interpretation of data presented in Fig. 3 difficult. The systems involving ST at 420°C serve to broaden the alkane distribution with respect to that in the absence of catalyst, whereas the distribution for systems involving JP at 420°C did not behave in a systematic manner. The increase in alkane chain length over K10 has recently been attributed to catalytic alkylation on the open, porous surface [29]. At 650°C, the tendency was towards the production of shorter alkanes which is probably related to an increase in the amount of cracking compared to isomerisation which takes place at elevated temperatures [38].

Figs. 4 and 5 also show that other low molecular weight species, particularly methylaromatics, were obtained yet the relative amount of aromatics produced decreased as the extent of acid leaching increased. This shift towards lower molecular weight and/or aromatic species was attributed to  $\beta$ -scission plus cracking and dehydrocyclisation, respectively [13,29]. In general, the catalysts decreased in their ability to produce aromatics as JP120 > JP240 > JP360; ST30 > ST120 > ST240. Moreover, at 420°C the selectivity over the ST and JP catalysts were significantly different whilst both the quantity produced and the selectivity were reduced in the dynamic process.

Clearly, the mildly activated clays produced the most aromatics but no molecules larger than ethyltoluene were identified in the catalytically transformed products which may be a consequence of the relative stability of the methylaromatics [6]. Although this agrees with Uemichi's work using silica-alumina

[5], it contrasts with results using the zeolite ZSM-5 ([13,39] where, in addition to toluene and the xylenes, benzene was clearly identified. Benzene was produced by the acid clays, but it co-eluted with several low boiling point species making quantitation difficult. Indeed, catalytic degradation over ZSM-5 produces large quantities of low molecular weight gases (C<sub>3</sub>–C<sub>4</sub>), because this zeolite prevents more than four carbon atoms from entering the channel network — a feature which is effectively exploited in the dewaxing process [40]. Nonetheless, ZSM-5 does produce aromatics when molecules, pre-cracked on the external surfaces, enter the channel network [7]. In a more detailed study than that of Uddin et al. [3], Ohkita et al. [39] correlated surface acidity with the products formed when thermally degraded polyethylene was passed over silica-alumina, of selected compositions. They found that at 400°C gas production increased with increased surface acidity while oil production decreased.

Songip et al. [41,42] showed that H-ZSM-5 was not suitable for the reforming of heavy oil derived from polyethylene even though it did not readily coke up. The gasoline produced had a good octane number, but the yield was low (20%) compared to the gas production (68%), whereas proton-exchanged (HY) and rare earth-exchanged (REY) zeolite-Y produced gasoline of similar quality with up to 30% less gas. HY contains a larger number of more acidic sites than REY leading to a lower gasoline yield (27 vs. 49%) and larger amounts of both gas (44 vs. 35%) and coke (6 vs. 3%). Thus, REY was the optimum choice because its bigger pore size allowed heavy oil in and it had fewer acid sites which resulted in a slower deactivation rate and less coke deposition when compared to HY [41,42].

Acid-activated clays have a larger number of milder acid sites than most zeolites [43] and they are predominantly Lewis acid sites after activation at high temperatures [44]. Consequently, their behaviour mimics that of REY and the large, unsaturated molecules produced during the thermal degradation of HDPE are cracked into smaller molecules. Dehydrocyclisation also occurs and aromatics are formed. Moreover, whilst cracking to small gaseous molecules does occur, particularly at 650°C it is low in comparison to that which occurs over the large number of strong acid sites in the microporous ZSM-5. Figs. 4 and 5 show that there was a shift in the products

formed over JP from toluene and xylenes, in the isothermal process, to xylenes and trimethylbenzene, in the dynamic process. These products are the same as found over silica–alumina [6].

The greatest proportional yield of aromatics and branched alkanes was obtained for clays with the least acid treatment which suggests that both processes relied in some way on small pores and high relative acidities (Table 2). The formation of branched alkenes from linear alkenes is essential to the provision of secondary carbenium ions which can then undergo the required ring closure and dehydrogenation reactions to produce aromatics. However, it is apparent that more aromatics were produced when the feed rate of the reactants was low and/or the residence time at the catalyst surface was long. In the current experimental configuration it is not possible to separate these two variables. However, it is clear that when rapid transport to and through the catalyst bed occurs then the proportion of aromatics was reduced in favour of branched alkanes. Uemichi et al. [6] also noted an increase in the aromatic/aliphatic ratio as the residence time increased.

Moreover, isomerisation is favoured over cracking at low temperatures [38]. These parameters combine to maximise the production of aromatics at low operating temperatures whereas branched alkanes are favoured at higher temperatures. When the extent of acid treatment is increased the surface area reaches a maximum and then begins to decline whilst the acidity decreases.

## 5. Conclusions

The thermal decomposition of HDPE up to 650°C yielded characteristic quartets of peaks assigned to *n*-alkanes, *1*-alkenes, *x*-alkenes and  $\alpha,\omega$ -dienes in the range C<sub>4</sub>–C<sub>22</sub>. Species of higher molecular weight than C<sub>22</sub> were not detected. All six catalysts converted the alkenes present in the thermally generated off gases into light gases, branched alkanes and aromatic species including good quantities of toluene, xylenes, tri- and tetramethylbenzenes. Ethylbenzenes and naphthalenes were produced to a lesser extent. More aromatics were produced at 420°C than at 650°C whereas the reverse was true for branched alkanes. The total conversion of HDPE increased with both the

extent of acid treatment and the process temperature, whereas the proportion of aromatics produced was greatest for catalysts prepared using short acid-treatment times at low process temperatures. Thus, there is considerable potential to control the product distribution by choosing appropriate combinations of acid-treatment of the catalyst and the process temperature.

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