A combined kinetic and mechanistic modelling of the catalytic degradation of polymers

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Abstract

Acid-catalysed hydrocarbon cracking reactions involve a large number of compounds, reactions and catalyst deactivation and are very complex. A new approach is presented that combines kinetic and mechanistic considerations which take into account chemical reactions and catalyst deactivation in the modelling of the catalytic degradation of polymers. The model gives a good representation of experimental results from the degradation of HDPE and PP over fluidised acidic catalysts. This model provides the benefits of product selectivity for the chemical composition such as alkanes, alkenes, aromatics and coke, in relation to the effect of structurally different polymer feeds, and the performance of the catalyst used. It is an improvement of the currently available empirical "lumping" techniques which usually are severely restricted in terms of product definitions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymer waste can be regarded as a potential source of chemicals and energy. Methods for recycling polymer waste have been developed and new recycling approaches are being investigated [1]. Chemical recycling, i.e. conversion of waste polymers into feedstock or fuels, has been recognised as an ideal approach and could significantly reduce the net cost of disposal [2]. Several reports [3–7] described the conversion of polymer waste by non-catalytic thermal degradation. Other reports address the role of acid catalysts in the catalytic degradation of polymers [8–13]. Although

the result of these studies has been the improvement of the catalyst, there is still a need to develop kinetic models to describe the experimental results and to facilitate the further development of a process to industrial scale.

Papers concerning kinetic modelling of catalytic process for polymer degradation have great limitations, which are shared with the study of other complex reaction schemes such as catalytic cracking and reforming. The kinetic models proposed in the literature can be grouped into (i) kinetic models based on thermal analysis of the weight loss curves [14–16], (ii) kinetic models based on reaction mechanism and elementary steps [17–19] and (iii) models with lumping schemes [20–23]. In the case of thermal analysis, the shortcoming is in general excessive simplification either in the assumed kinetic scheme or in the handing

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Nomenclature

$C(c)$	coke content (% w/w catalyst)
$k_{i,j}$	apparent rate constant of the individual reaction of formation of product i from jth reaction (min^{-1})
n_j	apparent reactor order of jth reaction
$r_{i,j}$	rate of the individual reaction of formation of product i from jth reaction (g (feed)/g (catalyst) min)
t	time (min)
W_r	weight fraction of the individual reaction of reactant r or evolution of product r

Greek letters

α	rate of activity loss with coke content (w/w)$^{-1}$
η	activity of the catalyst
η_j	activity of the catalyst of the individual jth reaction

Subscripts

a	aromatic (BTX) lump
c*	complex of molten polymer/catalyst
i	intermediates of olefins and carbenium ions
o	olefinic lump
o*	initial acid sites at time $t = 0$
p	paraffinic lump
r	coke lump
T	global apparent rate constant of formation of the olefinic lump, paraffinic lump, BTX lump and coke lump

of experimental data. Kinetic models with individual reaction steps lead to a great number of kinetic parameters, whose application for the simulation of industrial reactors is difficult. In the lumped kinetic models, the large number of individual constituents in a complex feedstock are grouped into the broad but measurable categories of compound classes, with simplified reaction networks between the lumps. These lumped models may be useful for the needs of reactor design, but there still exist some inherent limitations. Firstly, the approach often fails to extrapolate to different feedstocks because of composition differences within the same defined lumps. Secondly, coarsely lumped models cannot be utilised to interpret the

effects of catalyst properties on the phenomenological aspects of catalytic properties because fundamental catalytic reaction mechanisms are not incorporated into the kinetic scheme. Thirdly, insufficient detail exists in the lumped models to predict subtle changes in product properties.

Mechanistic considerations of catalytic degradation of hydrocarbons have largely been focused on small molecules ($<C_{16}$) rather than on macromolecules such as polymers. The literature available involving the mechanistic considerations for catalytic polymer degradation is rather scarce. For example, Ishihara and coworkers [10,24] gave only a qualitative mechanistic description by using intramolecular rearrangement of chain end secondary carbenium ions for the catalytic decomposition of polymers, but these results were not used to provide a kinetic model. The objective of this work is to use a kinetic/mechanistic model to study the production rates and product selectivity on the catalytic reactions of different polymers with various catalysts, and provide some basis to enhance the potential benefit of catalytic polymer recycling.

2. Experimental

2.1. Materials and experimental procedures

The polymers used in the experiment were pure high density polyethylene (HDPE; unstablised, MW $\approx$ 75,000, $\rho = 960.3\,\mathrm{kg\,m^{-3}}$, BASF) and pure polypropylene (PP; isotactic, MW $\approx$ 330,000, $\rho = 851.6\,\mathrm{kg\,m^{-3}}$, Aldrich). Both HDPE and PP were pyrolysed over zeolites (HZSM-5 and HUSY) and a Silica-alumina (SAHA) catalyst under identical reaction conditions. The catalysts employed and their preparation are described in our previous paper [13]. The particle size of both catalyst (75–120 μm) and polymer (75–250 μm) was chosen as being large enough to avoid entrainment. The catalyst was small enough to be adequately fluidised. A detailed description of the experimental system was given elsewhere [25]. Gaseous products were analysed using a gas chromatograph equipped with a thermal conductivity detector and a flame ionisation detector (FID). The solid remaining deposited on the catalyst after the catalytic degradation of the polymer

Table 1
Product distributions of HDPE and PP degradation at reaction temperature of 360°C over various catalysts[a]

Yield (wt.% feed)	HZSM-5		HUSY		SAHA	
	HDPE	PP	HDPE	PP	HDPE	PP
Gases (C_1–C_4)	64.1	67.5	34.8	37.1	30.3	22.5
Gasoline (C_5–C_9)	27.1	25.1	53.7	52.4	54.2	63.5
Liquid	2.3	2.3	3.2	3.5	3.4	4.4
Residue	4.5	3.7	7.1	6.2	12.1	9.4
Involatile	2.8	2.6	3.1	2.4	9.6	7.6
Coke	1.7	1.1	3.9	3.7	2.5	1.8
BTX	2.0	1.5	1.2	0.9	–	–
C_4 and C_5 hydrocarbons						
i-C_4H_{10}	8.4	10.6	13.2	11.8	1.6	0.7
n-C_4H_{10}	1.8	2.1	0.7	0.3	0.1	n.d
C_4H_8	26.7	24.7	11.3	16.6	20.9	17.9
i-C_5H_{12}	4.3	4.5	14.2	10.9	1.0	0.4
n-C_5H_{12}	0.7	0.7	0.3	–	n.d	n.d
C_5H_{10}	12.5	11.6	7.5	14.7	23.3	21.4

[a] Catalyst particle size = 75–120 μm, fluidising N_2 rate = 570 ml min^{-1} and polymer to catalyst ratio = 40% w/w; liquid: condensate in condenser and captured in filter; residue: coke and unconverted polymer; BTX: benzene, toluene and xylene; –: <0.01%; n.d.: not detectable.

were deemed "residues" and contained involatile products and coke. Mass balances were, in most cases, >90%. The amount and nature of the residues was determined by thermogravimetric analysis (TGA).

2.2. Experimental results

For simplicity, catalytic pyrolysis products are grouped together as hydrocarbon gases ($<C_5$), gasoline up to C_9 (C_5–C_9), liquids (condensate in condenser and filter) and residues (coke and products, involatile at reaction temperature, deposited on catalyst) to enable the overall pyrolysis processes to be described more easily. Table 1 summarise the products of HDPE and PP degradation over various catalysts. The bulk of the products observed were in the gas phase (>85 wt.%) with <5 wt.% liquid collected. The highest level of unconverted polymer was observed with SAHA, whilst the highest coke yields was observed with HUSY. HZSM-5 yielded the amount of C_1–C_4 and C_5–C_9 products, which were approximately 65 and 25 wt.%, respectively, with the highest level of BTX. However, HUSY gave the different C_1–C_4 and C_5–C_9 yields, which was approximately 35 and 55 wt.%, respectively, with about 12 wt.% of an *iso*-C_4 paraffin.

3. The model

3.1. Mechanistic aspects

The SEM studies previously [26] using a heated stage indicate that, for premixed polymer/catalyst particles, at temperatures around 300°C, the molten polymer is drawn into the spaces between particles and hence to active sites at the external surface of zeolite catalysts or in larger pores of amorphous materials. Surface reaction then produces lower molecular weight materials which, if sufficiently volatile at reaction temperature, can either diffuse through the polymer film, as products, or react further in the pores, including micropores, of zeolites. As a result, product distributions reflect features of the zeolite catalysts in relation to their pore systems and chemical composition. This is evident in the product distributions shown in Table 1. For example, comparison of HZSM-5 and HUSY in cracking HDPE shows the expected increase in bimolecular hydrogen transfer typical of the large ring, large cavity, *Y* structure versus the medium pore HZSM-5. This is reflected in the alkane/alkene ratios in the C_4 and C_5 products. In fact the pattern of the C_4 alkanes and alkenes is very similar to that observed in gas oil and gasoline cracking [27] and results can be explained in a similar manner.
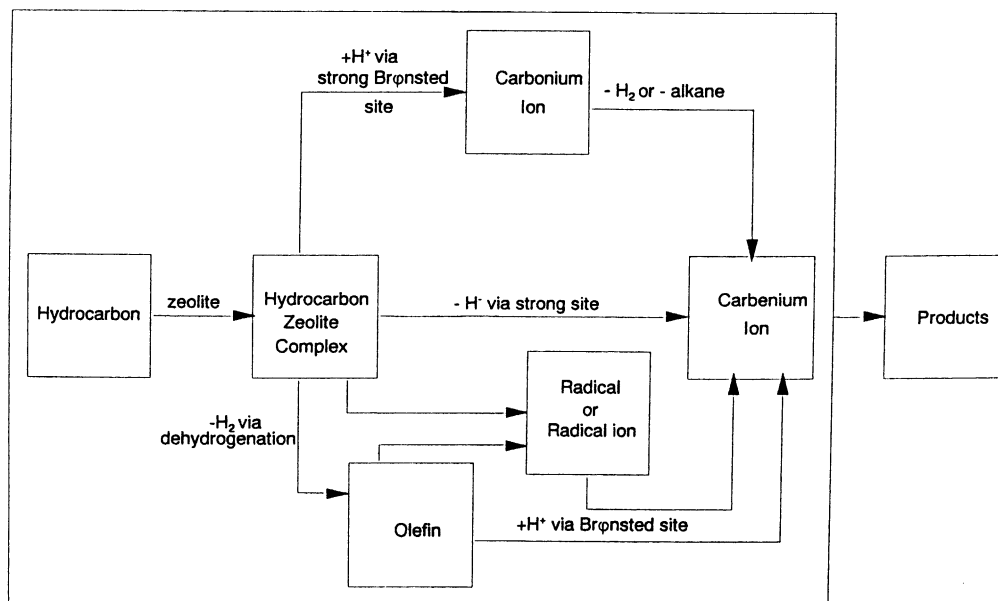
Fig. 1. A general mechanistic scheme representing hydrocarbon degradation in zeolites.

3.2. Combined mechanisms

A general mechanistic reaction scheme involving the discussion of the carbenium ion of catalytic cracking chemistry for the degradation of hydrocarbon (Fig. 1) has been proposed previously [27]. This representation is simplified regarding the formation of carbenium ions in that it concentrates on reaction paths rather than on surface species. Theoretical studies [28] suggest that, for the conversion of
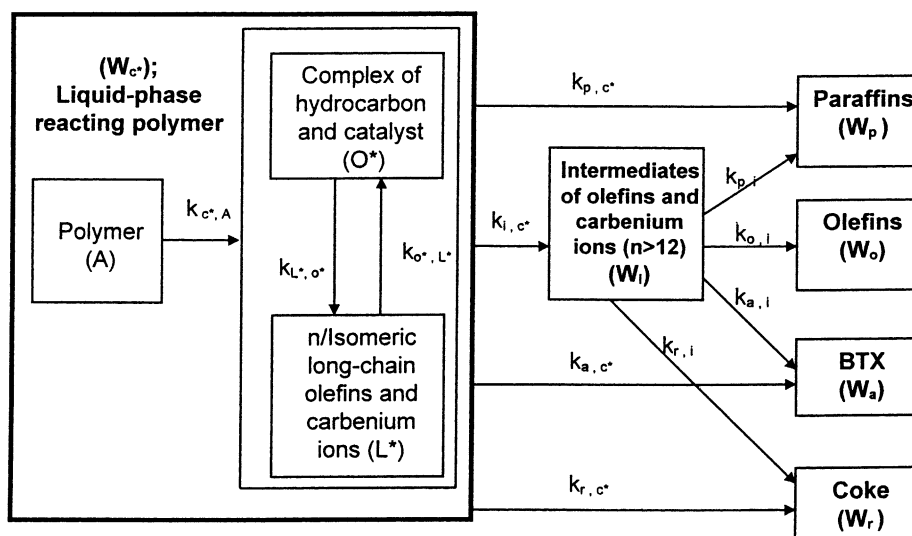

Fig. 2. A mechanistic and kinetic scheme representing polymer degradation over cracking catalysts.

hydrocarbons on active zeolites, reactions proceed via carbenium ions as transition states [29] (rather than as intermediates) and product distributions are also generally in agreement with carbenium ion studies, although there is still debate about the actual mode of scission [30]. In this paper, a kinetic/mechanistic model including the main mechanistic features and kinetic reaction schemes for polymer degradation over cracking catalysts is investigated (Fig. 2). The model uses the following assumptions.

1. The liquid-phase polymer. Initially, solid polymer is freely dropped into the reactor and immediately melts to disperse around the catalysts. The molten polymer, in contact with the catalyst particle forms a polymer/catalyst complex, reaction commencing at the surface. Polymer melting and spread times are negligible.
2. Evolution of intermediates. Scission reactions generate intermediates which include long-chain olefins and intermediate precursors for carbenium ions. The carbenium ions rapidly reach a steady-state concentration. Alkanes may be generated, via hydrogen transfer, and initially will be largely long-chain products. In general, the number of active sites limits the number of carbenium ion precursors.
3. Evolution of products. Once the intermediates are produced, further reactions could be expected to produce smaller chain olefins in equilibrium with surface carbenium ions, as well as alkanes, benzene, toluene and xylene (BTX) and coke. The equilibrium mixture of olefins and carbenium ions subsequently reacts further to produce the final products.

3.3. The reaction scheme and rate expressions

On the basis of the reaction pathway shown in Fig. 2, the rate of formation, $r_{i,j}$ of the product i from reactant r, through reaction j can be written as

$$r_{i,j} = k_{i,j} W_r^{n_j} \eta_j \tag{1}$$

where $k_{i,j}$ is the rate constant of the product i from the jth reaction, W_r the weight fraction of the reactant r present on the acid sites, η_j the catalyst activity decay of the jth reaction, n_j the reaction order of the jth reaction. An exponential decay function with activity

decaying as function of coke on catalyst was employed for HDPE on HUSY.

$$\eta = \exp[-\alpha \times C(c)] \tag{2}$$

where $C(c)$ is coke content deposited on the catalyst HUSY and α a constant, found to be 0.163 (% w/w)$^{-1}$ for HDPE [31]. For the model we consider, as an approximation, that α, in the deactivation process, can be taken as constant for both polymers and that the active sites are deactivated at the same rate for the acid catalysts studied. The activity decay, η_j, was assumed to be the same for all reaction steps with the activity proportional to the number of remaining sites.

$$\eta_j = \eta = \exp(-\alpha W_r) \tag{3}$$

where W_r is coke content deposited on the individual catalyst. Eqs. (4)–(9) were obtained assuming that reaction rates can be represented by simple first-order processes (i.e. $n_j = 1$) and catalyst deactivation involving six simultaneous equations. Initially, surface reaction forms a complex of molten polymer/catalyst. Thus, the rate of the consumption of the lumped liquid-phase polymer species (W_{c*}) can be written as

$$\frac{-dW_{c*}}{dt} = \eta(k_{i,c*} + k_{p,c*} + k_{a,c*} + k_{r,c*}) \times W_{c*} \tag{4}$$

Therefore, the formation of intermediates of olefins and carbenium ions ($n > 12$) can be expressed as

$$\frac{dW_i}{dt} = \eta[k_{i,c*} W_{c*} \\ -(k_{o,i} + k_{p,i} + k_{a,i} + k_{r,i}) \times W_i] \tag{5}$$

Similarly, the evolution of the olefinic lump (W_o), the paraffinic lump (W_p) the BTX lump (W_a), and the coke lump (W_r) are described as follows

$$\frac{dW_o}{dt} = \eta k_{o,i} W_i \tag{6}$$

$$\frac{dW_p}{dt} = \eta(k_{p,i} W_i + k_{p,c*} W_{c*}) \tag{7}$$

$$\frac{dW_a}{dt} = \eta(k_{a,i} W_i + k_{a,c*} W_{c*}) \tag{8}$$

$$\frac{dW_r}{dt} = \eta(k_{r,i} W_i + k_{r,c*} W_{c*}) \tag{9}$$

The mass balance can be written as

$$\frac{-dW_{c*}}{dt} = \frac{dW_i}{dt} + \frac{dW_o}{dt} + \frac{dW_p}{dt} + \frac{dW_a}{dt} + \frac{dW_r}{dt} \tag{10}$$

Eqs. (4)–(10) were numerically integrated by a fourth-order Runge–Kutta algorithm with Matlab (Version 4.2) to very the individual rate constants by minimising the sum of the squared deviations between calculated and experimental results. This gave values for the apparent rate constants.

4. Results and discussion

The kinetic/mechanistic model has been used to represent product distributions for the degradation of polyolefins over acidic catalysts under the fluidised bed reaction. As shown in Fig. 3, it shows that the
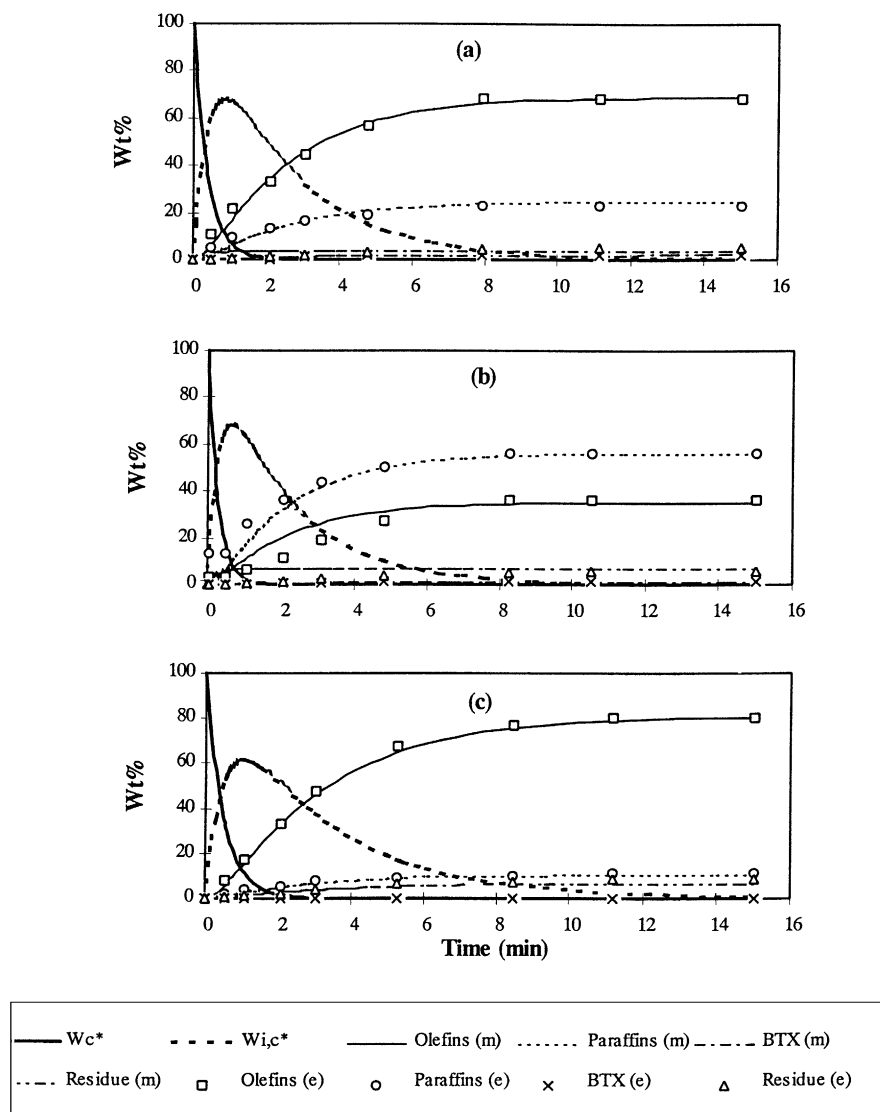

Fig. 3. Comparison of calculated (m) and experimental (e) results for the degradation of HDPE over (a) HZSM-5, (b) HUSY and (c) SAHA catalysts at 360°C (catalyst particle size = 75–120 μm fluidising N_2 rate = 570 ml min^{-1} and polymer to catalyst ratio = 40% w/w).

Table 2
Comparison of apparent rate constants for the degradation of HDPE over various cracking catalysts at 360°C[a]

Catalyst	$k_{i,c*}$ ($\times 10^{-2}$ (min^{-1}))	$k_{r,c*}$ ($\times 10^{-2}$ (min^{-1}))	$k_{p,c*}$ ($\times 10^{-3}$ (min^{-1}))	$k_{a,c*}$ ($\times 10^{-3}$ (min^{-1}))	$k_{o,i}$ ($\times 10^{-2}$ (min^{-1}))	$k_{r,i}$ ($\times 10^{-2}$ (min^{-1}))	$k_{p,i}$ ($\times 10^{-2}$ (min^{-1}))	$k_{a,i}$ ($\times 10^{-3}$ (min^{-1}))
HZSM-5	245.5	1.3	13	0.4	30.1	0.8	10.9	9.8
HUSY	329.3	2.8	8.6	0.3	18.6	2.3	25.7	6.6
SAHA	182.5	5.1	0.6	<0.1	31.5	2.1	2.7	<0.1

[a] Catalyst particle size = 75–120 μm, fluidising N$_2$ rate = 570 ml min^{-1} and polymer to catalyst ratio = 40% w/w.

calculated values using various catalysts are in good agreement with the experimental data.

4.1. Variation in product generation rates with catalysts

The apparent rate constants based on the model for various catalysts used in this study are summarised in Table 2. The generation of intermediates (long-chain olefins and carbenium ions) from the liquid-phase polymer is much faster than other reaction rates such as the generation of (i) the paraffinic lump ($k_{p,c*}$), (ii) the BTX lump ($k_{a,c*}$), and (iii) the coke lump ($k_{r,c*}$). The value of $k_{i,c*}$ is higher for zeolites (HUSY > HZSM-5) than for SAHA. Zeolites gave more intermediate stream about 70 wt.% compared with 60 wt.% with SAHA. It seems that zeolites (HZSM-5 and HUSY) are likely to form a polymer/zeolite complex and consequently to proceed the scission reaction further to generate the volatile products. This also suggests that the nature of the catalyst with zeolites is more effective in converting polymers into intermediates of volatile precursors than the amorphous SAHA.

The subsequent reactions for the generation the olefinic lump, paraffinic lump, BTX lump, and coke lump from long-chain olefins and carbenium ions lump was found to vary with the catalyst used. Higher

values of the apparent rate constant of paraffinic lump ($k_{p,c*}$) were observed in HUSY compared to in HZSM-5 and SAHA, while much higher value of the generation rate of residual lump ($k_{r,c*}$) was found in SAHA. For zeolites of HZSM-5 and HUSY, the generation of olefinic and paraffinic lumps is much faster than the generation of BTX lump and coke lump ($k_{r,i}$) For SAHA, the generation of the olefinic fraction ($k_{o,i}$) is much faster than the other values of the generation of paraffinic lump ($k_{p,i}$) and BTX lump ($k_{a,i}$).

4.2. Product selectivity changes with reacting conditions

In this work, the influence of polymer feed and catalyst type is evaluated. Table 3 shows product selectivity of olefins, paraffins, residual and BTX for the competition reactions from intermediate lump (long-chain olefins and carbenium ions). Product selectivity of degradation of both polymers degradation over various catalysts gives similar results on the structurally different polymer feeds. Comparison of zeolites in cracking of HDPE and PP shows an increase in olefinic selectivity with HUSY (39.4% versus 43.7%) and a decrease in paraffinic selectivity with HZSM-5 (25.6% versus 30.2%). The difference in the amount of olefinic product ($k_{o,i}/k_T$) for different

Table 3
Comparison of product selectivity for HDPE and PP degradation over various catalysts

Catalyst	HDPE[a]				PP			
	$k_{o,i}/k_T^1$ (%)	$k_{r,i}/k_T$ (%)	$k_{p,i}/k_T$ (%)	$k_{a,i}/k_T$ (%)	$k_{o,i}/k_T$ (%)	$k_{r,i}/k_T$ (%)	$k_{p,i}/k_T$ (%)	$k_{a,i}/k_T$ (%)
HZSM-5	70.3	1.8	25.6	2.3	65.2	2.2	30.2	2.4
RUSY	39.4	4.8	54.4	1.4	43.7	5.5	49.1	1.7
SAHA	88.6	3.8	7.6	<0.1	86.7	3.9	9.4	<0.1

[a] k_T^1: $k_{o,i} + k_{r,i} + k_{p,i} + k_{a,i}$.

catalysts is in the order SAHA (86.7–88.6%) > HZSM-5 (65.2–70.3%) > HUSY (39.4–43.8%). Product selectivity varied strongly dependent on catalysts type and structure. Compared with those of zeolites (HZSM-5 and HUSY), SAHA with large mesopores and low acidity resulted in a relatively low rate of bimolecular reaction to further react to produce paraffins. This also can be seen for zeolites (HZSM-5 = 2.3–2.4%; HUSY = 1.4–1.7%) produce a much higher selectivity to BTX than for SAHA (<0.1%).

The difference in product selectivity for zeolites can be seen with HUSY giving a higher selectivity for paraffins and coke than HZSM-5. However, HZSM-5 generates a much higher selectivity for olefins compared with HUSY. These results may reflect HUSY with the combination of 12 ring pore openings and larger internal supercages allow significant bimolecular reactions and yielded a paraffinic product (49.1–54.4%) and substantial coke levels (4.8–5.5%). The relatively low value (1.8–2.2%) of the $k_{r,i}/k_T$ (coke selectivity) suggests that bimolecular reactions such as hydrogen transfer, are sterically hindered within the 10 ring small channel of HZSM-5.

4.3. Discussion

Although results over a range of temperatures using a range of catalyst particle sizes has not yet tested to provide information in mass effects, the values of the kinetic constants and the model may be considered as an empirical one. It may be read with moderate interest by some works in polymer pyrolysis. Previous paper [25] shows a significant effect of nitrogen flow rate on the observed rates. This suggests that mass transfer from the outer surface of the catalyst particles may affect the calculated rate constants. Mass transfer rates in fluidised beds are known to be slower than rates in fixed bed reactors. For the mechanism used in this study, the polymer coating the particles is stated to be liquid, and for the reactions that occur on the interior pore surface the situation would seem to be completed. Gaseous products are forced out to have diffused in the macroporos and produced on the interior surface. A fuller paper is being developed from the mass and heat transfer effects on different reacting conditions and the behaviours of catalyst deactivation as related to the structure of catalysts and their acid sites.

An important challenge in the process modelling effort is the development of reliable kinetic equations for processes with complex feedstocks. A kinetic/mechanistic model is proposed, and for use to study the catalytic degradation of polymers and to optimise the potential benefit of catalytic polymer recycling. This model takes into account mechanistic considerations in relation to chemical composition (alkanes, olefins, aromatics and coke) and catalyst deactivation for the chemical reactions that occurred in the catalytic degradation of polymers. These materials (alkanes, olefins, etc.) are present in various molecular weight ranges and, consequently, can be used to define lumps based on the chemical behaviour of each group, and to account for chemical reactions. The kinetic rate constants, representing chemical reactions between lumps, are then no longer purely empirical but they represent the overall kinetics of the possible reactions in the lumped components.

5. Conclusion

This paper outlines some recent results relevant to the conversion of polymers for the production of potentially valuable hydrocarbons and fuels and also attempts to apply a model for the mechanism and kinetics of catalytic degradation of polymers. A combined kinetic and mechanistic model giving chemical information, applicable to the fluidised-bed reactions, was used to predict production rates and product selectivity for the catalytic degradation of polymers. The model based on a reaction scheme for the observed products and catalyst deactivation in relation to chemistry has been developed. This model gives a good representation of product selectivity and product distributions for catalytic polymer recycling and also provides an improvement of the empirical "lumping" techniques.

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