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Experimental and kinetic studies of the advantages of coke accumulation over Beta and Mordenite catalysts according to the pore mouth catalysis hypothesis

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ABSTRACT

Coke formation inside heterogeneous reactors is an important industrial problem that leads to reduced catalyst efficiency. However, this study aims to prove the benefits of coke build-up in improving catalyst performance. The formation and decomposition of coke on six different zeolite structures was studied. The dissociation kinetic model of the spent catalysts during the toluene alkylation with 1-heptene inside a stainless-steel autoclave reactor at different temperatures was carried out. Various techniques (XRD, XRF, TPO, CHNS and TGA-DTG) were used. It was found that the conversion and selectivity of the desired product were higher on the parent H-mordenite and the dealuminated H-beta catalysts with conversions of 85.3% and 84.67%, respectively, at a 360 min reaction time. This was attributed to the reduction of the ratio of hard:soft coke. It is confirmed that the decomposition activation energies of hard coke, 140.1–202.6 kJ/mol, are much higher energies than those of soft coke, 89.9–118.7 kJ/mol. It is also noted that the hypothesis of pore mouth catalysis is dominated by non-polyaromatic coke on the surface of the H-beta catalysts, while the hypothesis is dominated by polyaromatic coke on the surface of the H-mordenite catalysts.

1. Introduction

In the past few decades, the importance of linear alkyl methylbenzene in the production of household detergents has increased, especially at the end of 2019 when the corona-virus epidemic swept most of the world [1]. Linear alkyl methylbenzene is a critical industrial feedstock in the production of detergents and many other chemicals such as dyes, inks, synthetic fibres and pesticides [2,3]. Therefore, it is necessary to study the manufacture of this product and work to overcome the obstacles facing its production. Hence, finding the most suitable catalysts, raw materials and operating conditions for the manufacturing process are the main challenges that can be addressed to increase the production of this intermediate product. Although the employ of homogeneous catalysts gives high conversion and high yield of products, they cause several problems for the environment such as the use of hazardous chemicals, equipment corrosion and pollution [4]. Therefore, the optimal solution was to find alternatives to replace the homogeneous materials in order to address their associated problems. Heterogeneous catalysts emerged as a successful alternative, especially because of their attractive features for use in the alkylation reaction such as acidity, activity and shape selectivity [5]. Of all the heterogeneous catalysts, zeolites possess most of the properties required in alternative catalysts, mainly product selectivity [6,7]. The selectivity of the alkylation products over the zeolite catalyst showed an almost two-fold

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percentage increase compared to the non-zeolite catalysts [8]. The type and nature of the zeolite catalyst are the important factors that influence the distribution of heptyl-methylbenzene isomers [9]. Large pore zeolites with 2D and 3D topology such as mordenite, beta, and faujasite zeolites have been utilized to produce alkyl-methylbenzenes through aromatics alkylation with linear olefins [10–12]. Magnoux et al. [13] employed three types of zeolite catalysts, H-faujasite, H-mordenite and H-beta, in the toluene alkylation with 1-heptene. They investigated the effect of zeolite properties on both the conversion of 1-heptene and the selectivity of linear alkyl-methylbenzene products. They concluded that the acidity is the main parameter responsible for the activity of the zeolite. However, the structural pores control the rate of diffusion of the products from the micropores of the zeolite. Da and co-worker [14] studied the pore opening effect of HY and H-beta zeolites during the alkylation of 1-dodecene and 1-heptene with toluene. They demonstrated that H-beta zeolites trapped products inside their pores because they have small pore openings compared to HY zeolites and therefore the amount of accumulated coke in the H-beta zeolite was higher than in the HY zeolite and this meant that the H-beta activity was lower than when using the HY zeolite.

Three isomers of linear heptyl-methylbenzene (2-, 3- and 4- heptyl-methylbenzene) are obtained via toluene alkylation with 1-heptene over different types of zeolite catalysts [15]. In addition, 2- and 3-heptene can be obtained from double bound shifts of 1-heptene. Among the three heptyl-methylbenzene isomers, 2- heptyl-methylbenzene is the favourable product because it has high biodegradability compared with the other two isomers [16].

Even though zeolite catalysts have many advantages, they also have negative aspects, such as deactivation, which is the main problem that heterogeneous catalysts in general and zeolites in particular can face [17,18]. Zeolite deactivation is the main drawback that effects zeolite activity, selectivity and stability. Deactivation is a result of coke accumulation throughout a chemical reaction [19]. The coke is the main reason that poisoning of the acid sites occurs, by blocking the zeolite apertures through the toluene alkylation with 1-olefin [15]. It is a result of the deposition of heavy by-products that are formed through the side reactions such as olefin polymerisation and dimerisation of mono-heptyl-methylbenzene to form bi- and tri-heptyl-methylbenzene. Coke is formed as a result of the precipitation of bulky alkylation products and/or heavy by-products that block the pores of the zeolite as a result of the low turnover rate of these components leading to deactivation of the zeolite catalyst [20]. Nevertheless, these components can form during the reaction as intermediate components, in which case they are called 'Coke Precursor'. During the alkylation of toluene with mono-heptene, bi- and tri-heptyl-methylbenzene polymerise within the pores of the zeolite and deactivate the catalyst [21]. Da et al. [9] investigated the influence of alkylation products that polymerised inside the zeolite micropores during the alkylation of toluene with 1-heptene over H-faujasite zeolite. They found mono-, bi- and tri-heptyl-methylbenzene acted to block the apertures of zeolite pores thereby limiting the desorption of alkylation products from zeolite pores, which led to reduced activity of H-faujasite zeolite. However, Guisnet [15] demonstrated that the presence of excess toluene during the reaction is interesting to treat the deactivated catalyst by removing the coke molecules through the trans-alkylation that occurs near the pore mouth and even inside the super-cages. On the other hand, some studies have recently focused on the beneficial effects of coke deposits [22–25]. Frequently, the activity and selectivity of any catalyst is rapidly reduced through the early stages of the reaction as a result of deactivation that acts to block the most internal pores. In fact, the hypothesis of pore mouth catalysis can be applied as an accepted phenomenon to illustrate that the catalyst still retains most of the activity and stability [26,27]. Pore mouth catalysis is defined as the phenomena of permanence of efficacy active sites located nearby the pore edge until the substrate molecules are physically adsorbed despite the presence of blockages in other internal active sites [28]. Indeed, the isomerisation and alkylation reactions are less influenced by the formation of coke precursors because the reaction takes place at the pore mouths or on the external surface near the pore mouths [29]. Oh et al. [30] used beta and mordenite zeolite catalysts in the hydrolysis of Inulin, and concluded that pore mouth catalysis plays a major role in improving the conversion of Inulin. In addition, they showed that the presence of mesopores (with a diameter of 2–50 nm) formed during zeolite modification act to enhance pore mouth catalysis and the external surface area, compared to the primary micro-pores ($\leq$ 2 nm). Understanding the kinetics of coking is important for understanding catalyst deactivation and designing catalysts as well as processes in which deactivation is minimized. The type of coke, such as soft or hard coke, is one of the main factors affecting catalyst deactivation. The pore mouth catalysis hypothesis depends on several variables, such as; the type of coke, the location of the coke and the nature of the coke. Therefore, the study of the kinetics of coking is of interest in order to identify the type of coke according to the decomposition temperature, activation energy values and the decomposition rate of the coke [31,32]. The mechanism of coke decomposition is complex because many thermal reactions occur concomitantly [33]. The activation energy was obtained and evaluated according to the common isoconversion methods, which depends on the reaction conversion. Although the TGA suffers from the partially overlap peaks, it is widely recommended for kinetic study via deconvoluted these superimposed peaks [34,35]. Two independent reactions are the most appropriate description for the decoking model in this field [36,37]. Few of the studies that have emerged have paid attention to the kinetics of decoking of deactivated catalysts because the reaction contains a complex mechanism [38,39]. Nevertheless, there is a lack in the literature about using a thermogravimetric analyser for a kinetic study of the thermal decomposition of coke formations during the alkylation of toluene with 1-heptene, and it is relationship with the hypothesis of pore mouth catalysis.

In the present study, the hypothesis of pore mouth catalysis was verified by the activity, selectivity and stability of H-mordenite, H-beta and their modified catalysts during the alkylation of toluene with 1-heptene inside a high-pressure autoclave reactor. The main objective of this study is to demonstrate the usefulness of coke formation during the reaction in enhancing catalyst performance. Therefore, the effects of zeolite framework structures on pore mouth catalysis behaviour and the amount of coke accumulated have been extensively studied. In other words, the role of coke (that is, the ratio of hard:soft coke accumulated) during the reaction time was used to investigate the zeolite pore mouth catalytic mechanism. A comparison of experimental results and model prediction results showed that the multiple decomposition reaction kinetic models used in this work are reliable and can be used to mimic the TGA-data for the decoking process and thereby distinguish between soft and hard coke and estimate the kinetic parameters of coke decomposition.

2. Experimental

2.1. Materials

The chemicals used in this work are 1-heptene of 98% purity (Acros Organics). Toluene (99.5%) and ethanol ($\geq$99.8%), were obtained from Sigma-Aldrich. *n*-Pentane was provided at a purity of 99.8% from VWR. The catalysts used are beta zeolite in hydrogen form (i.e., acidic form) and mordenite zeolite in ammonium form, which are all supplied by Alfa Aesar. The ammonium-mordenite zeolite was converted to hydrogen form by calcination at 500 °C for 240 min. While the traditional methods using acid leaching and base leaching were followed to treat the parent Beta and Mordenite zeolites in the medium of 1 M HCl and 0.025 M NaOH, respectively and under reflux conditions of 85 °C for 60 min.

2.2. Catalyst characterisation

The X-ray diffraction (XRD) instrument used was STOE STADI P

CuKα1, with a radiation wavelength of 1.54 Å. Tests were carried out at room temperature, 2θ between 2 and 100, scan speed was 10° min^{1}, run time was about 28 min, tension was 40 kV and current 35 mA. XRD data were analysed using X'pert highscore-plus software. The X-ray fluorescence (XRF) spectrophotometer used was the PANalytical Zetium using a plastic analysis cup and the Omnian37He application. Nitrogen adsorption/desorption was measured with a Micromeritics 3Flex at 196 °C, using the Brunauer, Emmett and Teller (BET) and Horvath-Kowazoe methods. Pre-analysis, the powder zeolite samples were outgassed in a quartz tube at 200 °C for 720 min using a vacuum furnace. 3Flex Version 3.02 software was employed for this measurement. The PerkinElmer TGA 4000 instrument was used to measure the amount of coke formed during the chemical reaction from room temperature to 400 °C using nitrogen gas then from 400 to 800 °C using air at a heating rate of 10 °C min-1 and a gas flow rate of 20 mL min-1 for both ranges. The coke percentage was determined via Eqs. (1 and 2):

$$coke\%(soft) = \frac{W_{200} - W_{400}}{W_{400}} \times 100 \quad (1)$$

$$coke\%(hard) = \frac{W_{400} - W_{800}}{W_{800}} \times 100 \quad (2)$$

($W_{200,\ 400,\ 800}$: specimen weight at 200 °C, 400 °C and 800 °C)

The temperature programmed oxidation (TPO) instrument connected to a thermal conductivity detector (TCD) was a Micromeritics Chemisorb 2720 with a Eurotherm 2416 temperature controller. It was used to classify the types of coke formed on the zeolite through the reaction. Approximately 50 mg of specimen was placed in a quartz U-tube reactor, and then put in a furnace. 25 mL min-1 of helium was used to decontaminate the sample for 30 min. Then, the furnace temperature was raised from room temperature to 850 °C at a rate of 10 °C min-1 using 5% oxygen/helium and maintained for 30 min. Organic elemental analysis (CHNS) is employed to characterise the coke deposits during the chemical reaction, using Flash 2000 with pure oxygen at 900 °C. It was used to calculate the hydrogen/carbon (H/C) ratio.

2.3. Experiment set-up

The work was carried out using a 45 ml stainless-steel autoclave from Autoclave Engineers, as illustrated in Fig. 1. The feed consisted of a 3:1 M mixture of toluene and 1-heptene, with a total volume of 3 mL of 1-heptene and 7 mL of toluene over 0.3 g of zeolite catalyst that was preheated at 150 °C for 120 min to activate the zeolite in each experiment. The reaction was initiated under conditions of 90 °C, stirrer speed of 300 rpm and at atmospheric pressure. Five different reaction times were employed; 30, 60, 120, 240 and 360 min. At the end of each experiment, the reactor was placed in ice water to immediately stop the reaction. The filtration process under vacuum conditions was used to separate the produced liquids from spent zeolite catalyst. GC-FID (Thermo Scientific, TRACE 1310) with a DB-5HT column was employed for quantitative analysis, whereas GC–MS (Shimadzu, GCMS-QP2010 SE) with a DB-1MS column was used for qualitative analysis. The solid catalyst was washed with 20 ml of n-pentane for half an hour to remove the adsorbents from the inter pores of the zeolite catalyst, and then the catalyst was dried at 120 °C for 720 min. 1-heptene conversion was calculated and the selectivity for all linear heptyl-methylbenzene was also calculated according to Eqs. (3 and 4):

$$conversion\% = \left[\frac{no.of\ moles\ of\ 1-heptene\ consumed}{no.of\ moles\ of\ 1-heptene\ introduced}\right] \times 100 \quad (3)$$

$$Selectivity\% = \left[\frac{no.of\ moles\ of\ monoheptyl-methylbenzene}{no.of\ moles\ of\ 1-heptene\ consumed}\right] \times 100 \quad (4)$$

3. Results and discussions

3.1. Catalyst characterisations techniques

3.1.1. X-ray diffraction

X-ray diffraction (XRD) was used to study the structural framework of zeolites before and after the dealumination and desilication modifications. Fig. 2 shows the XRD patterns of H-beta and H-mordenite as well as their modified forms (i.e. dealumination and desilication). Interestingly, the diffraction peaks of the modified samples are similar to the patterns of the fresh zeolites. The peaks of the XRD patterns are shifted either to a higher value of 2θ as a result of dealumination or to a smaller value as a result of desilication, as shown in Fig. 2 (b and d). After the desilication treatment, the dimension of unit cell is expanding as a result of silicon expelling from the zeolite lattice, so the 2θ at 7.335 (for H-beta) and 9.375 (for H-mordenite) are shifted slightly to the left-hand side. Similar results were obtained in an earlier study by Wardani et al. [40]. In contrast, the 2θ for dealumination is shifted to the right-hand side as a result of shrinking of the unit cell dimension that happened as a result of the removal of aluminium atoms from the zeolite framework. The same results were shown previously by Al-Zaidi and co-workers [41]. These results provide clear evidence of the success of the modification procedures for zeolite structures without collapse of the crystalline composition.

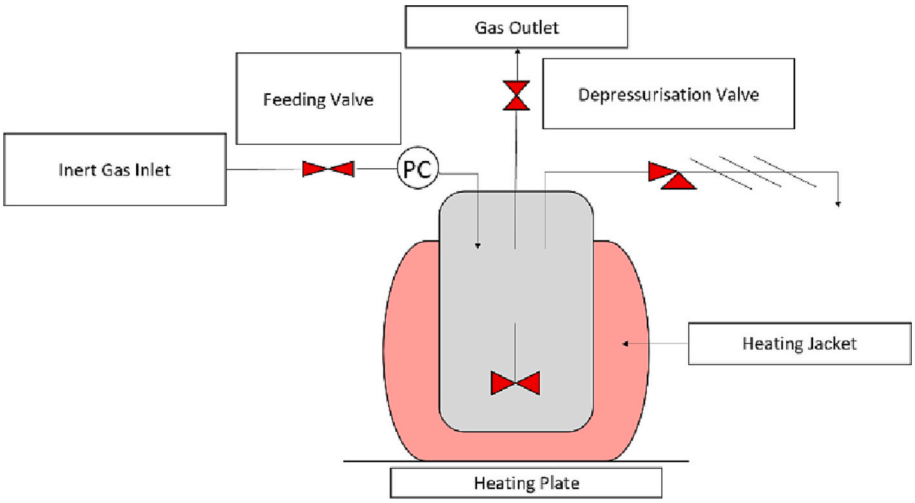

Fig. 1. Batch reactor schematic diagram.

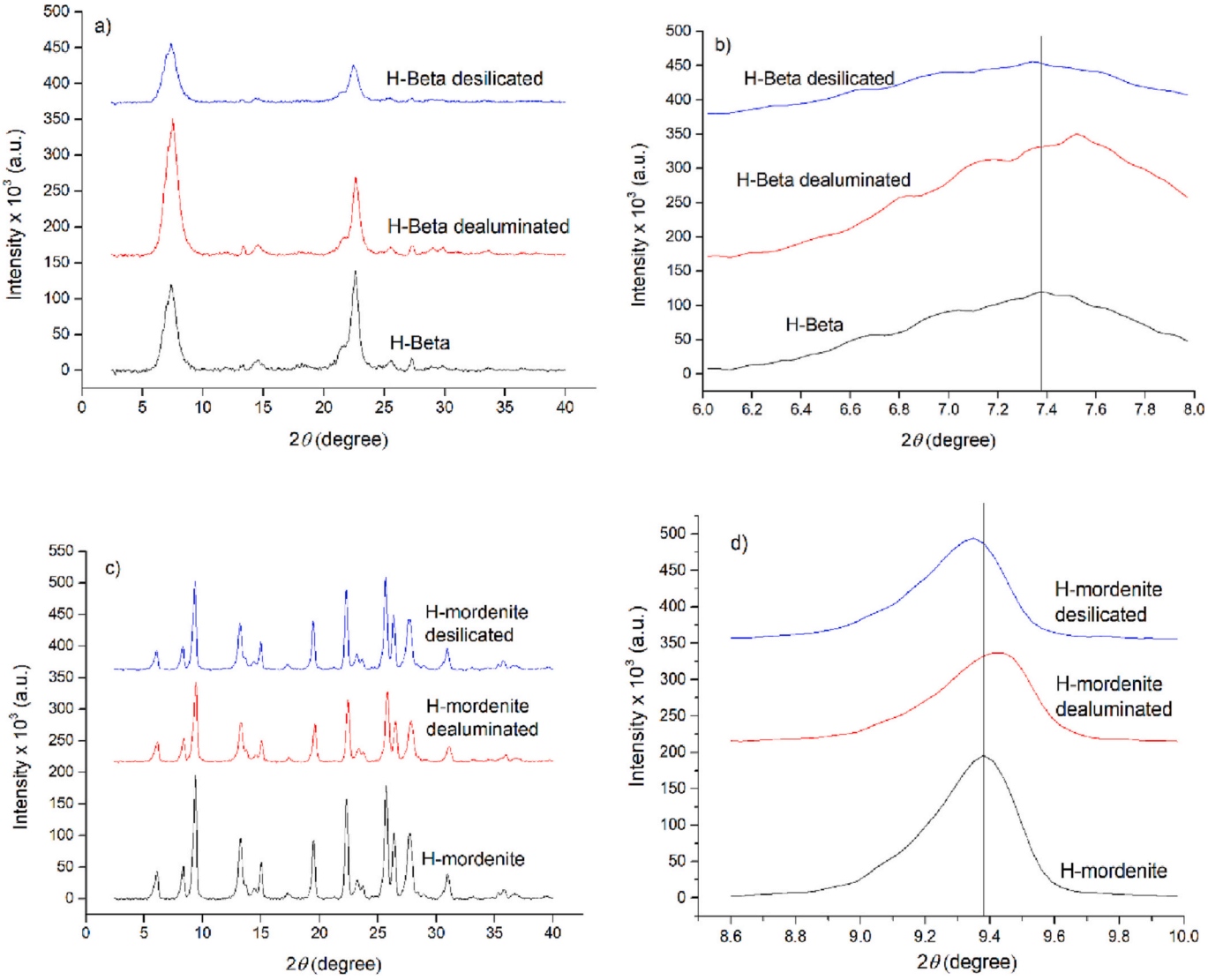

Fig. 2. XRD patterns of parent and modified a) and b) H-beta; c) and d) H-mordenite zeolite catalysts.

3.1.2. *Textural properties and X-ray fluorescence*

It can be seen in Table 1, both dealuminated H-beta and dealuminated H-mordenite achieved a decrease in the BET surface area and pore volume with a slight increase in the pore size of the micro-apertures. In contrast, desilicated H-beta and desilicated H-mordenite showed an increase in the BET surface area. Moreover, both desilicated catalysts displayed improvements in mesopore volume and pore size compared to the parent zeolites. This occurs naturally due to the process of opening the structural framework of the zeolite as a result of removing a portion of the silicon atoms [41]. The bulk silica/alumina (Si/Al) ratio of parent, dealuminated and desilicated H-mordenite and H-beta were characterised using XRF. Although the XRF analysis showed a low-alumina content within the H-beta zeolite framework (i.e., it seems more siliceous than the H-mordenite zeolite), there is little variation between the results of the H-beta parent and the desilicated sample and similar observations were made for the H-mordenite parent and desilicated samples. These results confirm the absence of a deep desilication process, which helped to not collapse the framework structure of the zeolites. However, BET has confirmed that the treatment method increases the mesoporosity of the zeolite samples. On the other hand, for both types of zeolites, the influence of the dealumination treatment was clear, as shown by the significant increase in the Si/Al ratio (i.e. decrease in the acidity of the zeolite samples).

Table 1
Nitrogen adsorption and XRF of parent and modified zeolite catalysts.

Zeolite	Si/Al (XRF)	S_{BET} (m^2 g^{-1})	V_{tot} (cm^3 g^{-1})	V_{mic} (cm^3 g^{-1})	V_{meso} (cm^3 g^{-1})	$d_{p\ mic}$ (Å) Horvath-Kowazoe
H-beta	209.8	613	0.326	0.209	0.117	5.28
Dealuminated H-beta	493.8	478	0.315	0.193	0.112	5.34
Desilicated H-beta	203.4	631	0.332	0.116	0.216	5.57
H-mordenite	20	491	0.286	0.189	0.097	6.26
Dealuminated H-mordenite	38.2	389	0.168	0.137	0.091	6.29
Desilicated H-mordenite	17.1	503	0.293	0.148	0.145	6.71

3.1.3. *Thermogravimetric analysis (TGA)*

Fig. 3 shows the TG and DTG diagram of the decoking of spent catalysts that were obtained from the current study exhibit two main peaks. The first zone is between 200 and 400 °C and is designated as the soft coke region, whereas the second zone covers the temperatures from 400 to 800 °C and is designated as the hard coke region [38]. As can be seen in Figs. 3a-c, H-beta parent and its modified samples show a maximum

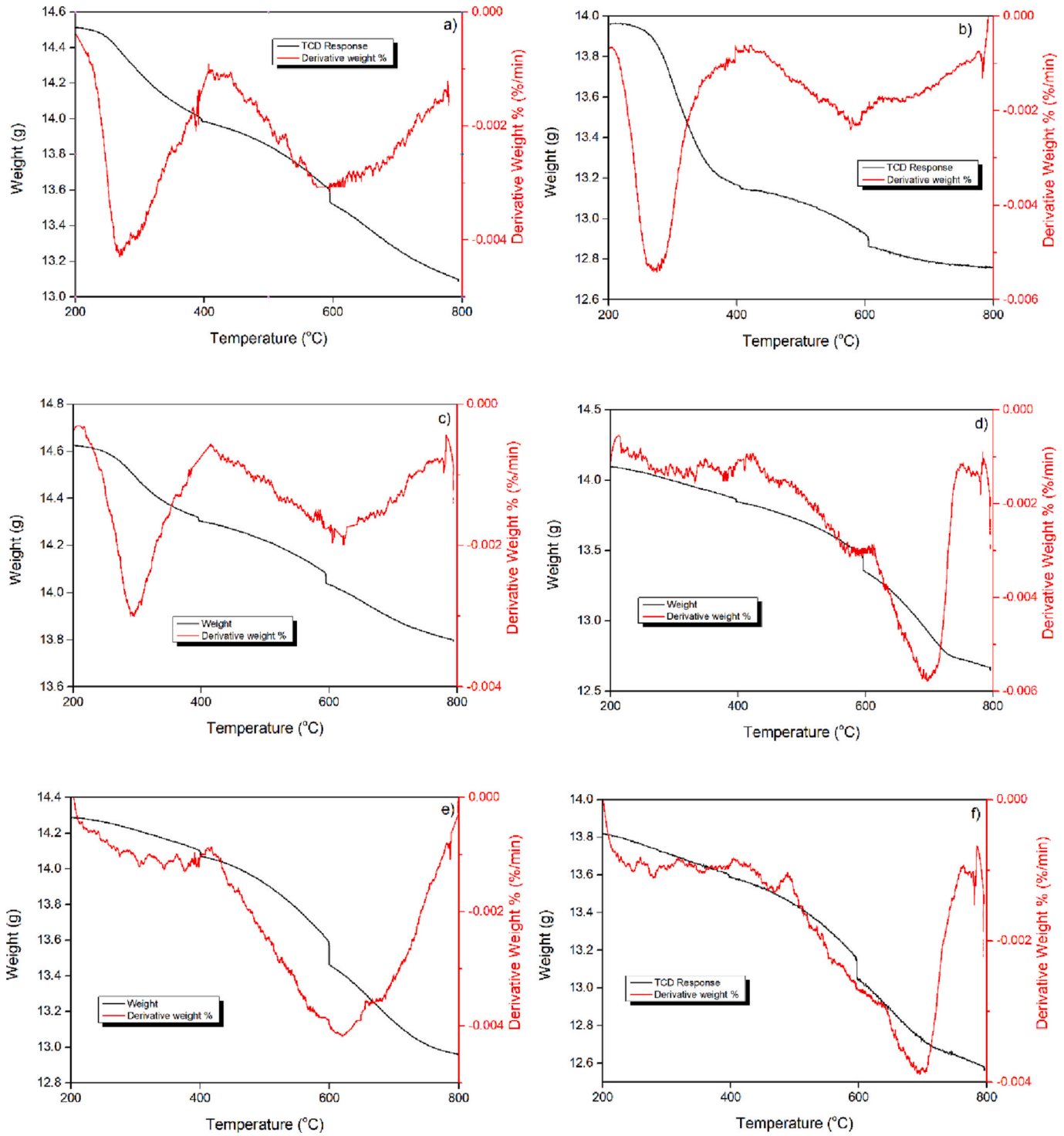

Fig. 3. TGA-DTG plots of the (a) H-beta, (b) dealuminated H-beta, (c) desilicated H-beta, (d) H-mordenite, (e) dealuminated H-mordenite, (f) desilicated H-mordenite zeolite.

peak in the first zone at around 280 °C, which represents the high percentage of soft coke. In contrast, parent, dealuminated and desilicated H-mordenite samples display the biggest peak in the second zone at about 700 °C with the main decomposition of hard coke (as seen in Figs. 3d-f).

Fig. 4 demonstrates the effect of oxidation temperature on the type of coke formation through the time-on-stream over H-beta, H-mordenite and their modified forms. In general, H-beta and its modified forms showed a noteworthy amount of soft coke. However, the hard coke increased with time-on-stream, and represented the main type of coke over the H-mordenite and its treated forms. In general, it can be seen that the percentages of coke reduced after the desilication treatment on both the H-beta and H-mordenite catalysts, possibly owing to the formation of mesopores within their structures as previously shown in the nitrogen adsorption-desorption results. Similarly, the dealuminated samples also demonstrated lower coke formation compared to the parent samples, especially within the H-beta catalyst due to the Si/Al ratio being more than doubled after the dealumination modification, as

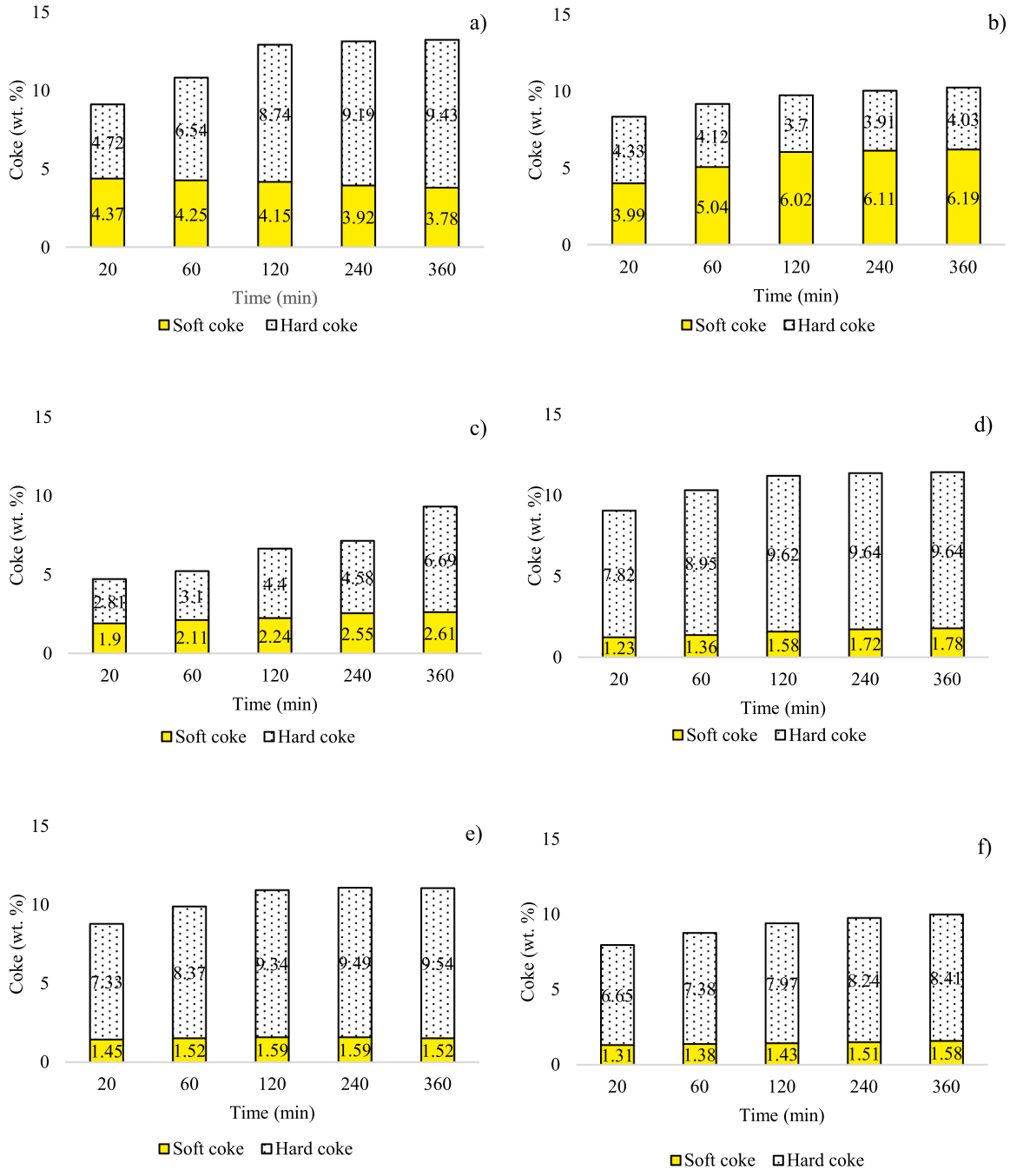

Fig. 4. The weight percentages of coke types obtained by TGA at various times: (a) H-beta, (b) dealuminated H-beta, (c) desilicated H-beta, (d) H-mordenite, (e) dealuminated H-mordenite, (f) desilicated H-mordenite.

earlier explained in the XRF results. The found results are previously confirmed by other authors [42,43]. This modification made the catalyst less acidic and less conducive to coke formation within its structural framework. Through these results, it is clear that both the base and acid treatment processes on the lattice of the catalysts led to a decrease in the amount of coke accumulated on their surface during the reaction.

Fig. 5 shows that the hard:soft coke ratio seems to be decreased with time over H-beta dealuminated and H-mordenite, whereas the ratio was increased over other types of catalysts. These interesting results confirm the hypothesis of pore mouth catalysis presented around the reaction mechanism, and also explain the strange behaviour of the effect of the coke precursor species formed on the acidic sites of the catalysts during the reaction despite the presence of blockages in other internal active sites. The pore mouth catalysis suggested that the accumulated coke can minimise the activity of the strong acid sites thereby reducing the overall acid sites density. On the other hand, this coke is played as active sites near the pore mouth of the catalyst and catalysing the reaction in the direction of selective enhancement.

3.1.4. *Elemental analysis (CHNS)*

Table 2 shows the content of hydrogen and carbon and the hydrogen/carbon (H/C) mass ratio that was obtained by elemental analysis for H-beta, dealuminated H-beta, desilicated H-beta, H-mordenite, dealuminated H-mordenite and desilicated H-mordenite. For all

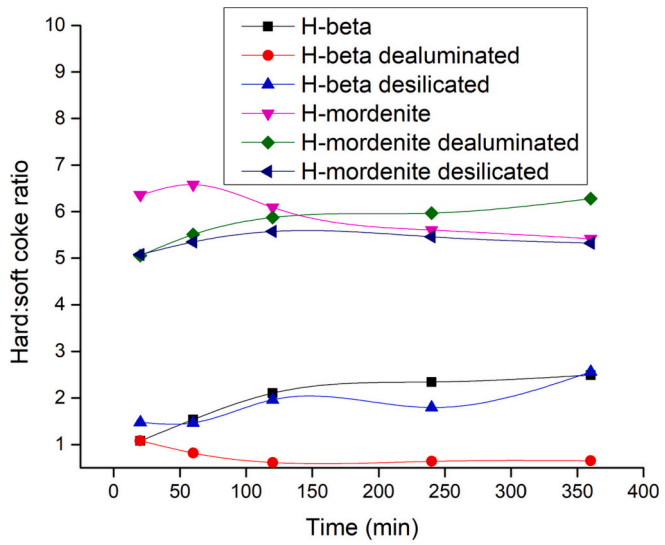

Fig. 5. Hard:soft coke ratios for fresh and modified H-beta and H-mordenite analysed by TGA at various reaction times.

Table 2
The Hydrogen/carbon mass ratio via the CHNS elemental analysis for H-beta and H-mordenite and their modified samples at reaction time of 360 min.

Zeolite	%H (wt%)	%C (wt%)	H/C mass ratio
H-Beta	2.1 ± 0.07	7.3 ± 0.14	0.29 ± 0.07
Dealuminated H-Beta	2.6 ± 0.35	6.2 ± 0.21	0.42 ± 0.14
Desilicated H-Beta	1.3 ± 0.14	1.8 ± 0.14	0.72 ± 0.07
H-Mordenite	2.3 ± 0.07	22.7 ± 0.28	0.1 ± 0.21
Dealuminated H-Mordenite	2.0 ± 0.14	18.2 ± 0.28	0.14 ± 0.42
Desilicated H-Mordenite	2.2 ± 0.01	14.7 ± 0.14	0.15 ± 0.07

samples, the carbonaceous deposits formed due to condensation and rearrangement during all transformations of hydrocarbon compounds throughout the alkylation reaction showed a low H/C mass ratio and this indicates hydrogen-deficient coke. Bauer and Karge [44] classified coke into two types depending on the H/C mass ratio; hydrogen-rich coke with a H/C mass ratio >1 and hydrogen-deficient coke with an H/C mass ratio <0.8. It can also be seen that the structure of the coke formed on H-mordenite and its modified forms is mainly polyaromatic coke with a high carbon content, while H-beta and its modified forms is mainly less polyaromatic coke with a low carbon content. These results agree with those obtained from XRF on the acidity of the catalysts as well as the results of TGA on the type of coke precipitated during the reaction.

3.1.5. Temperature programmed oxidation (TPO)

TPO is widely employed to illustrate the behaviour of coke reactivity of the active sites of zeolite catalysts. Fig. 6 shows the TPO profiles of post-reaction coke formation within the surface of H-beta, dealuminated H-beta and desilicated H-beta as well as H-mordenite, dealuminated H-mordenite and desilicated H-mordenite samples. In general, the main difference in the TPO profiles between these zeolites is similar to what has been shown previously by the TGA test. Namely, it is observed that the TPO profiles of H-beta and its modified samples exhibit a broader peak combined with soft and hard coke and the soft coke appears as a small shoulder while hard coke is expressed by the wider peak. On the other hand, the H-mordenite and its modified samples contain higher carbon content as previously proven in Table 2, and therefore two separate peaks appear in their TPO profiles that express the type of coke accumulated within them according to the changes in the nature of the coke.

The TPO profiles of dealuminated H-beta and desilicated H-beta compared with the parent H-beta show a decrease in maximum temperature and intensity. The maximum temperature peaks are shifted to the left with a lower order of coke formation. In fact, the TPO profile of the beta catalyst is attributed to the presence of structurally ordered coke; however, it tends to be non- and/or less-polyaromatic after the modification [45]. On the other hand, for H-mordenite sample and its modified forms, there is a noticeable difference in the maximum temperature, which is located at approximately 320 °C for the parent H-mordenite sample. For the dealuminated sample, soft coke was shifted to the left of lower pyrolysis, with a maximum temperature of about 300 °C, and the maximum temperature of the desilicated sample was around 290 °C, as shown in Fig. 6. This probably indicates the presence of less ordered coke. The type of coke in these sites tends to be amorphous carbon or polyatomic coke [46]. However, the TPO profile of the H-mordenite and its modified forms at almost 680 °C look like hard coke profiles, with a slight reduction in the maximum pyrolysis temperature after the dealumination and desilication treatments to approximately 670 °C. All these profiles fall into graphitic-like carbon [47].

3.2. Experimental reaction results

3.2.1. Catalyst activity of toluene alkylation

The variation in zeolite pore structure, surface area and pore size distribution were studied using two different types of zeolite catalysts, namely H-beta and H-mordenite with different Si/Al ratios. The data obtained for the catalytic performance of parent, dealuminated and desilicated H-beta in toluene alkylation with 1-heptene at 90 °C inside a batch reactor is illustrated in Fig. 7. At a reaction time of 30 min, it shows that the lowest conversion was achieved when using H-beta zeolite, which is probably because the coke that formed acted to

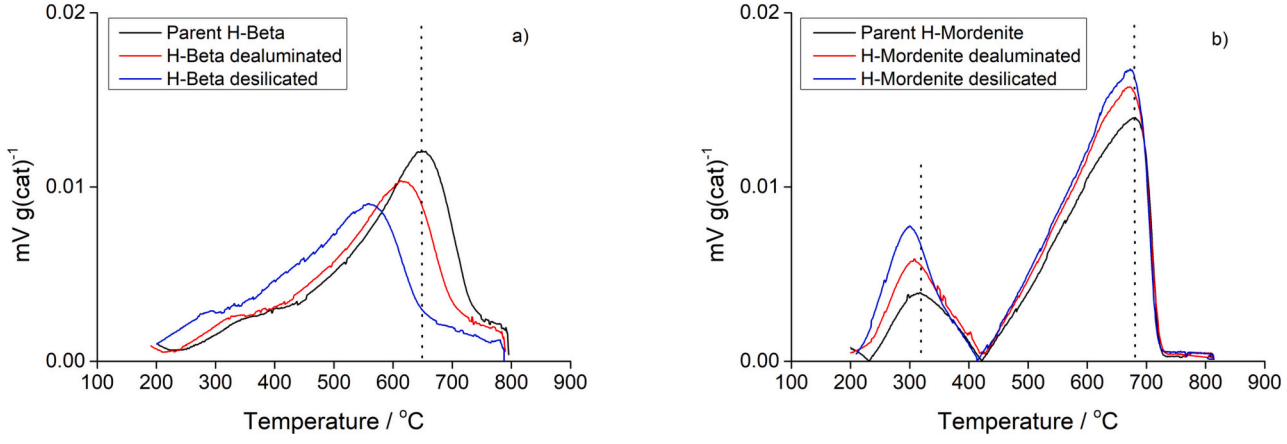

Fig. 6. TPO profiles of the a) H-beta and its modified forms and b) H-mordenite and its modified forms after the alkylation reaction.

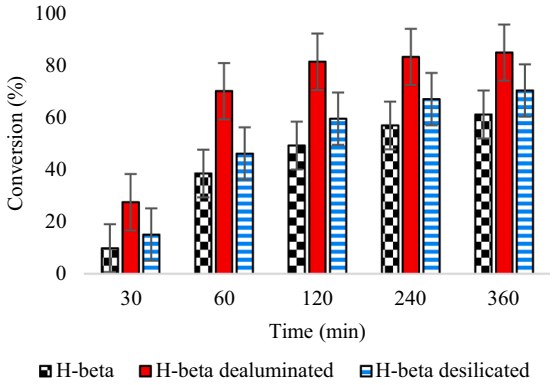

Fig. 7. Conversion during toluene alkylation with 1-heptene over H-beta, dealuminated H-beta and desilicated H-beta.

deactivate the zeolite quickly by blocking their pore openings. This result is in agreement with the result obtained by Cao et al. [48]. Moreover, it is clear that the conversion of 1-heptene using dealuminated H-beta was higher than the conversion when using the H-beta parent, possibly because the Si/Al ratio was dramatically increased compared to the unmodified sample which means the acidity decreased and this led to a reduction in the ratio of hard:soft coke accumulated, as shown in Fig. 5. The same conclusion was made by Craciun et al. [49]. Furthermore, it can be seen that the conversion of 1-heptene over desilicated H-beta increased compared with the conversion achieved using the parent zeolite as a result of a more open structure being created after the de-silication treatment, as confirmed by the BET results. The accumulation of coke led to enhanced shape selectivity of bulky product molecules through the pore mouth. Although the amount of coke that formed on the desilicated sample was lower (i.e. increased the H/C mass ratio) than that on the parent and dealuminated H-beta, the conversion of 1-heptene over the desilicated sample was lower than when using the dealuminated H-beta sample. This could be owing to the fact that the percentage of hard coke is higher than the percentage of soft coke when using the desilicated sample (i.e. there is an increased hard:soft accumulated cokeratio) and it continues to grow during the time on stream, but its rate is still slower than that in the case of the parent H-beta sample, as shown in Fig. 5, and thus gives a higher conversion compared to it. These results illustrate the roles that can be played by the type and amount of coke build-up within the catalysts and their effect on the reaction products.

Fig. 8 shows the conversion of 1-heptene over H-mordenite and its modified samples (e,g, dealumination and desilication). The conversion showed a linear growth over the reaction time to reach about 85% at 360 min while using the H-mordenite parent. This is likely to happen because it has a high concentration of acid sites as a result of the low Si/Al ratio and this supports the formation of hard coke. In spite of the fact that the coke that formed on the H-mordenite zeolite has a high percentage of hard coke (i.e.it has a higher carbon content), the low percentage of soft coke played a vital role in supporting the increase in the conversion, especially after 120 min when the amount of hard coke has become constant at 9.64 wt.% (i.e. reduced the ratio of hard:soft accumulated coke, as shown in Fig. 5) and analogous results were shown by Horňáček et al. [50].

In addition, it can be remarked that the activity of the modified samples which seems to be decreased after treatments, as shown in Fig. 8. This may be due to the change in the Si/Al ratio from that of the parent catalyst to each of the modified samples, which led to a change in the acidity and the distribution pattern of the acidic sites within the structural framework of the catalysts. The change in the Si/Al ration may also have led to changes in the surface area and the size of the pore openings, as previously documented by Triantafillidis and his coworkers [51] which led to an increase in the possibility of hard coke formation. Thus, it can be seen in Fig. 5 that the ratio of hard:soft coke accumulated has increased during the time on stream, especially with the use of the H-mordenite dealuminated catalyst. The ratio of hard:soft coke also accumulated when using the desilicated H-mordenite catalyst. However, the H-mordenite parent catalyst showed a decrease in hard:soft coke ratio over the reaction time. On the other hand, it can be seen that maximum conversion was achieved at a much faster rate on the H-mordenite catalyst compared to H-beta and this can be attributed to the higher acidity and activity of H-mordenite, and thus it is preferred for use with the alkylation reaction of toluene with 1-heptene compared to the H-beta catalyst. In fact, Beta zeolite has a complex structure consisting of a three-dimensional network, while Mordenite has a single channel system and is considered more suitable for adsorption and catalysis processes due to the stringent purity requirements that these applications demand.

3.2.2. Alkylation selectivity

Fig. 9 describes the selectivity of 2-heptyl-methylbenzene over parent, dealuminated and desilicated H-beta. The selectivity of 2-heptyl-methylbenzene when employing the H-beta zeolite shows the smallest selectivity because of the small pore size compared to other catalysts used for this type of reaction. Hence, its channels do not provide adequate space for the formation of bulky molecules within the micropores of the 3D channels, and the reaction probably takes place on the external surface of the zeolite, as confirmed by Magnoux et al. [13]. The selectivity seems to be constant at around 10%, which might be related to the formation of coke that deactivates most of the active sites responsible for the production of heptyl-methylbenzene isomers. Indeed, pore blockage occurs early in the onset of the reaction, and the

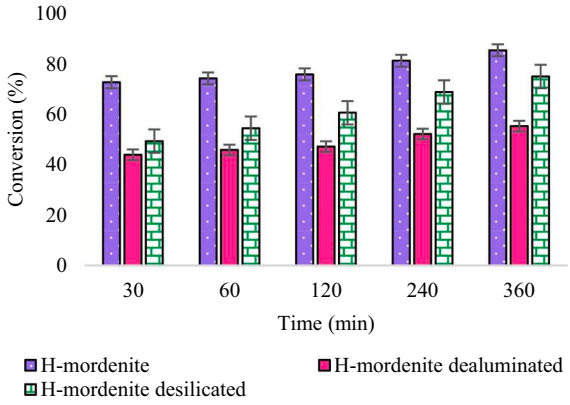

Fig. 8. Conversion during toluene alkylation with 1-heptene over H-mordenite, dealuminated H-mordenite and desilicated H-mordenite.

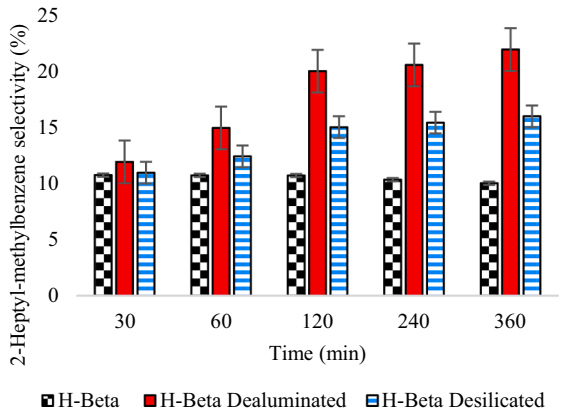

Fig. 9. Selectivity of 2-heptyl-methylbenzene during toluene alkylation with 1-heptene over H-beta, dealuminated H-beta and desilicated H-beta.

selectivity decreases slightly according to the phenomena of pore mouth catalysis. This result is consistent with that found by Wang et al. [32], they concluded that the production of iso-paraffins using SAPO-11 occurred in either at the pore edge or the region which is located near the pore mouth. At 120 min reaction time, the selectivity of the dealuminated H-beta catalyst was increased about 50% compared to the parent H-beta catalyst. The comparison between H-beta parent and the dealuminated H-beta at the same conversion ~74% reveals; 2-heptyl-methylbenzene selectivity over the H-beta parent was around 10%, while it increased to about 15% using the dealuminated H-beta. This improvement in selectivity ascribed to the enhancement of textural properties after dealumination treatment and this is clearly reflected in the results of the analysis of TGA, TPO and CHNS-elements by reducing the amount of coke and changing the type of coke to be softer with increasing the H/C ratio, as previously shown in the coke analysis results. Similar results were obtained in the study conducted on other reaction by Wang et al. [52]. The selectivity of 2-heptyl-methylbenzene using desilicated H-beta increased compared to the H-beta forms due to the formation of a mesoporous structure within a microporous structure as a result of the desilication modification, as shown in Table 1. The selectivity is improved up to a reaction time of 120 min and becomes almost double beyond this time due to the formation of coke. 2-heptyl-methylbenzene selectivity is meant here as a desired product, whereas, the 3-heptyl-methylbenzene selectivity remains at a lower level of about 4% which is probably owing to deactivation of the acid sites, which are responsible for the production of side products and act as active centres at/or near the pore mouth of the zeolites. Andy et al. [53] offered similar interpretations of their findings. From the above, it can be concluded that coke plays a beneficial role in improving the selectivity of catalysts throughout the reaction.

Fig. 10 demonstrates the selectivity of 2-heptyl-methylbenzene over parent, dealuminated and desilicated H-mordenite. In general, the parent sample shows the highest selectivity compared to the modified samples. This is a result of H-mordenite having a suitable pore size within its framework which desorbs the 2-heptyl-methylbenzene isomers that have a molecular size <5.3 Å [16], and this contributes to the increase in the 2-heptyl-methylbenzene selectivity througha higher shape-selectivity towards this product [50]. Additionally, the selectivity of the dealuminated H-mordenite sample was reduced compared to the parent sample owing to the increase in Si/Al ratio and a decrease in surface area, which led to the deactivation and blockage of the acid sites responsible for 2-heptyl-methylbenzene production. Although the rate of selectivity decreases with the reaction time on the surface of the parent and desilicated H-mordenite, it slightly increases on the surface of the dealuminated H-mordenite catalyst, as shown in Fig. 10. Once

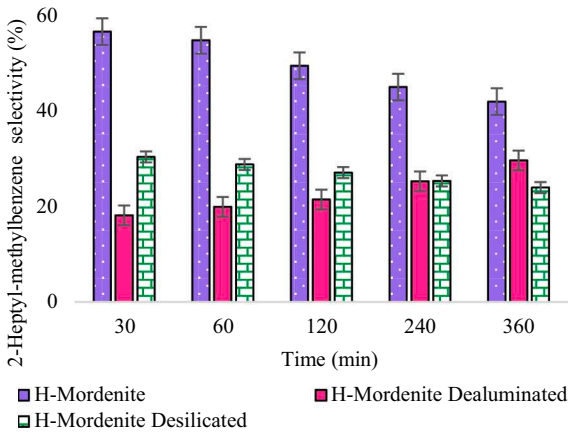

Fig. 10. Selectivity of 2-heptyl-methylbenzene during toluene alkylation with 1-heptene over H-mordenite, dealuminated H-mordenite and desilicated H-mordenite.

again, all these results can be attributed to the role of coke formation which is acting to reduce the acidity of the zeolite catalyst and its stability at different levels with reaction time, in addition to the pore mouth presumption. In other words, the rapid and high increase of the hard:soft coke ratio with the continuation of the reaction time over the dealuminated H-mordenite catalyst, as shown in Fig. 5. A similar conclusion was shown previously by Wiedemann et al. [54]. Likewise, the selectivity of the desilicated H-modified zeolite catalyst was lower than that of the parent catalyst, in spite of the percentage of hard:soft ratio is relatively the same on the surface of both catalysts. This can be related to the hypothesis of pore mouth catalysis, as the distribution and type of coke accumulated can played a significant role in determining the shape selectivity over the catalyst surface. Finally, the comparison between parent and desilicated H-mordenite showed that 2-heptyl-methylbenzene selectivity over the H-mordenite was about 50% at 120 mins, while selectivity was less than about 25% over the desilicated H-mordenite at 360 mins (i.e. almost twice the conversion rate). Similar results were obtained formerly by Horňáček et al. [55].

3.3. Coke decomposition reactions model

3.3.1. Kinetic analysis

The fundamental rate equation which is used in all kinetic studies is expressed in Eq. (5), where k is defined as the kinetic constant of the reaction while the temperature dependence is expressed by the Arrhenius equation in Eq. (6), where f(α) is the reaction model.

$$\frac{d\alpha}{dT} = k(T)f(T) \tag{5}$$

$$k(T) = A\mathrm{e}^{-E/RT} \tag{6}$$

Eq. (5) expresses the degree of conversion, dα/dT, at a constant temperature. The degree of conversion, α, represents the amount of decomposed sample at time t, and is described in Eq. (7),

$$\propto = \frac{m_i - m_a}{m_i - m_f} \tag{7}$$

$$\frac{d\alpha}{dT} = Af(T)\mathrm{e}^{-E/RT} \tag{8}$$

Where, ma, mi and mf are the actual, initial and final mass of the sample during the experiment. Coke decomposition reaction Eqs. (1 and 2) can be described also by Eq. (8).

Eqs. (9 and 10) describe non-isothermal TGA experiments with linear heating rate where β = dT/dt. In these equations, A, Eα, R, T, α, t, k(T), and f(α) are: frequency factor (s^{-1}), activation energy (J/mol), gas constant (8.314 J/mol·K), temperature (K), conversion, time (s), rate constant and the reaction model, respectively.

$$\frac{d\alpha}{dT}\frac{dT}{dt} = Af(T)\mathrm{e}^{-E/RT} \tag{9}$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta}f(T)\mathrm{e}^{-E/RT} \tag{10}$$

Eq. (11) can be used to represent the decomposition of materials with a narrow range of decomposition temperatures. For the materials with a wide range of decomposition models, a multi reactions model (as seen in Eq. (12)) can be applied to represent the rate of decomposition. This model assumes that the total rate of decomposition is equal to the sum of the single material decompositions.

$$\alpha = \sum_{i}^{N} \alpha_i \tag{11}$$

$$\frac{d\alpha_i}{dT} = \frac{A_i}{\beta}f(T)\mathrm{e}^{-E_i/RT} \tag{12}$$

The multi-step successive model analyses the kinetics of the coke and biomass pyrolysis based on the one-step global model. This model always divides the pyrolysis into a series of stages according to the temperature and mass loss, prior to obtaining the kinetic parameters. By comparison of the errors obtained from these models, reaction-order model $f(\alpha) = (1- \alpha)^n$ was found to be the most appropriate to represent the coke decomposition; therefore, this model was applied to simulate TGA results. In addition, after identifying the f(α) function, the pre-exponential factor (A), apparent activation energy (E_α) and the power (n) were numerically evaluated by using a stochastic optimization method. The correlation coefficient (R^2) was estimated to evaluate the performance of the two reaction models developed in this study as expressed in Eq. (13) [56,57]:

$$R^2 = 1 - \frac{\sum_{i=1}^{N} \left(y_{exp,i} - y_{pred,i}\right)^2}{\sum_{i=1}^{N} \left(y_{exp,i} - \overline{y}_{exp}\right)^2} \quad (13)$$

It is expected that the decoking reaction may include two major reactions because the spent zeolite contained different kinds of coke. Therefore, the two parallel independent reactions model is selected to represent the experimental results and to overcome the overlapping which results from the de-convoluted curves. The comparison between the experimental and the predicted data is shown Fig. 11, and Table 3 lists the seven kinetic parameters that were employed to express the decomposition process. In general, there is an extremely conformable fit between the experimental data and that predicted from the two-step

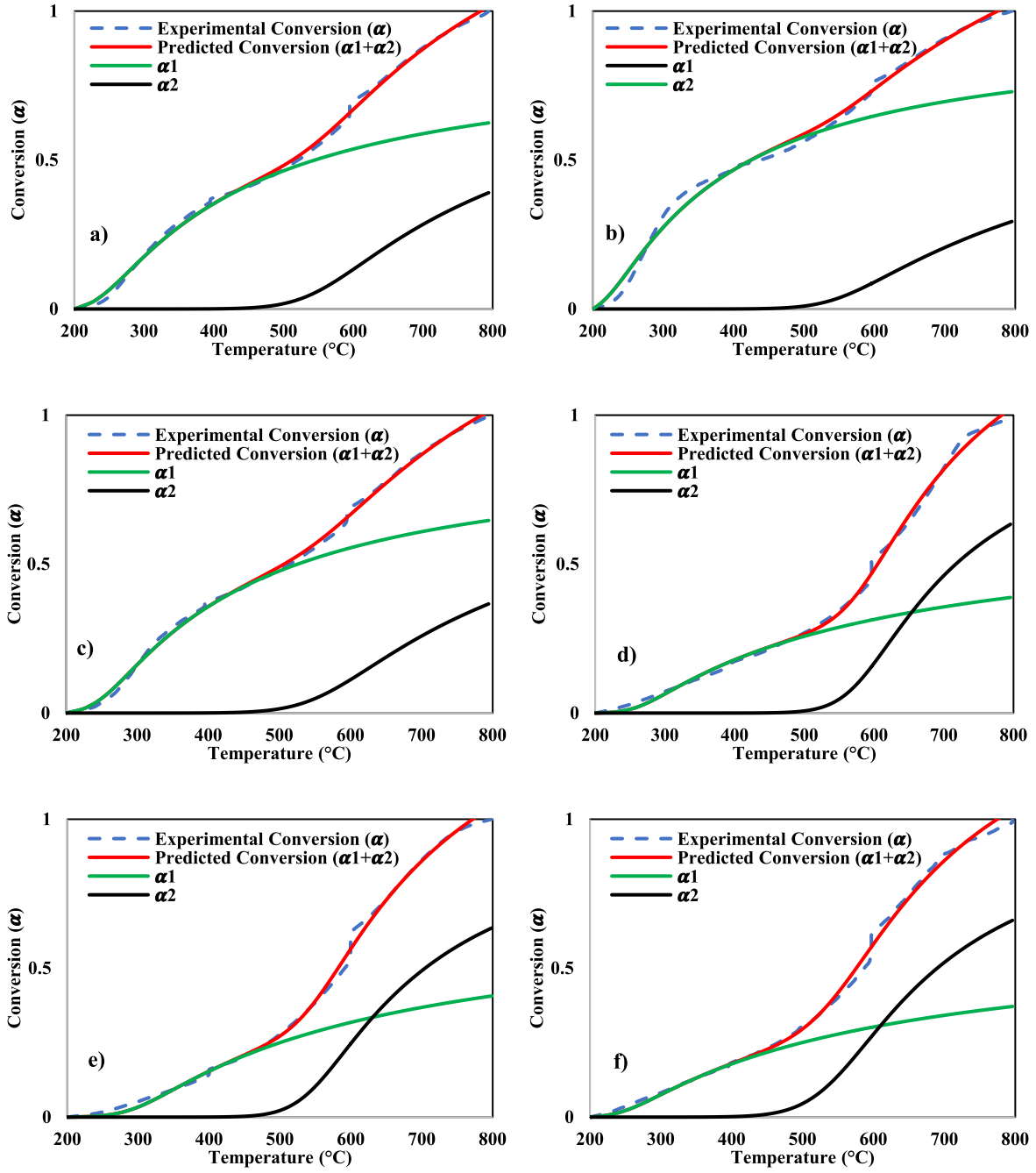

Fig. 11. The relative weight fraction α derived from the toluene alkylation with 1-heptene over: (a) H-beta, (b) dealuminated H-beta, (c) desilicated H-beta, (d) H-mordenite, (e) H- dealuminated mordenite, (f) desilicated H-mordenite zeolite.

Table 3
TGA results of Kinetic parameters of TGA.

Zeolite	A_1 (1/min)	A_2 (1/min)	E_1 (kJ/mol)	E_2 (kJ/mol)	n_1 (−)	n_2 (−)	R^2 (−)
H-beta	46.5×10^6	0.44×10^8	89.9	145.7	13.5	11.8	0.9980
Dealuminated H-beta	184.6×10^6	3.9×10^8	103.8	158.5	17.3	12.4	0.9937
Desilicated H-beta	170.2×10^6	0.15×10^8	97	140.5	13.1	11.6	0.9983
H-mordenite	142.3×10^6	1.5×10^{11}	118.7	202.6	30.7	9.2	0.9969
Dealuminated H-mordenite	23.1×10^6	0.7×10^{11}	99.3	190.1	22	8.1	0.9964
Desilicated H-mordenite	70.6×10^6	0.5×10^8	96.8	140.1	28.2	5.9	0.9955

1: soft coke, 2: hard coke

reactions model. α1 and α2 represent the conversion factor for the removal of soft and hard coke, respectively. According to TGA simulation results, the hard coke decomposition is started at the temperature within the range of 450–500 °C. Table 3 summarizes the effect of the kinetic parameters on the zeolite framework structure on weight percent of soft coke and hard coke depending on TGA simulation results. For H-beta, dealuminated H-beta and desilicated H-beta catalysts, the soft coke ratio is higher than that of hard coke, and is different from the accumulated coke over H-mordenite, dealuminated H-mordenite and desilicated H-mordenite catalysts where it is noted that the soft coke ratio is lower than that for hard coke.

Table 3 shows the activation energy of both parent and modified zeolite catalysts. For all the samples, it can be seen that the activation energy values of the second reaction are always higher than that obtained from the first reaction, where the E1 values are between 89.9 and 118.7 kJ/mol which is lower than the range of f E2 which are between 140.1 and 202.6 kJ/mol. Results from calculations of a mathematical model conducted on coke deposited on catalysts or this reaction using the TGA test where not found in the available literature, to enable a comparison of the data of this mathematical model with it. However, a comparison was made with similar data of other researchers. Ren and co-worker [39] indicated the kinetic parameter values of coke oxidation that derived from both asphaltenes and oil at different coking temperatures as the following: A1 = 1.92 × 107 1/min, A2 = 9.57 × 107 1/min, E1 = 115.34 kJ/mol and E2 = 124.17 kJ/mol. Generally, it can be recognized that the activation energies (that is, E1 and E2) of the coke decomposition of the H-beta and modified H-beta catalysts were almost lower than those of the H-mordenite and modified H-mordenite catalysts, indicating that the H-beta catalyst requires less energy for activation than H-mordenite catalysts. From the kinetic results listed in Table 3, it can be seen that there is a good agreement with those previously obtained from TGA analysis where the largest amount of soft coke was accumulated on H-beta and its modified samples and most of the amount of hard coke was accumulated on H-mordenite and its modified samples. Hard coke is known to require higher activation energies for decomposition. This result is also consistent with the results of the CHNS test, in which the H/C mass ratio is high on the surface of H-beta and modified H-beta catalysts, compared to that on the surface of H-mordenite and modified H-mordenite catalysts. In addition, according to the pre-exponential factor, soft coke can be decomposed quicker than hard coke which needs high decomposition energies and this is confirmed by the low value of activation energy which indicates that the reaction rate becomes faster, as mentioned earlier by Ahmed, et al. [38]. It is interesting that the decomposition activation energy values for the first reaction of soft coke on all types of catalysts are lower than the decomposition activation energy values for the second reaction and this supports the phenomenon of pore mouth catalysis because it plays a crucial role in increasing the selectivity of the heptyl-methylbenzene isomers despite the increase in accumulated coke. The higher the decomposition activation energy values mean, in turn, that the rate of coke formation during the reaction time is slower. It is noted that the values of decomposition activation energies obtained by using dealuminated H-beta catalyst for the first and second reactions amounted to 103.8 and 158.6 kJ/mol for soft and hard coke, respectively, which are higher than that for other Beta zeolite samples In addition, the values of decomposition activation energies obtained using H-mordenite catalyst for the first and second reactions amounted to 118.7 and 202.6 kJ/mol for soft and hard coke, respectively, which are higher than that for other Mordenite zeolites samples. The experimental results previously gave the highest conversion and the highest selectivity of the desired product on the surface of these two catalysts (i.e. dealuminated H-beta and H-mordenite), and this reinforces the hypothesis of the role of accumulated coke, as it is noted, as in Fig. 5, that the ratio of hard:soft coke accumulated during the time on stream decreased only on the surface of these two catalysts compared to other catalysts. This conclusion can give evidence that the hard:soft coke ratio during the reaction time is the criterion that can be relied upon in determining the results of conversion and selectivity on the catalyst surface. Moreover, the reaction order (n) of the first reaction is always greater than that of the second reaction which is inversely proportional to the values of the activation energy. A higher reaction order indicates excellent agreement between the experimental results and the predicted results. Similarly, high values of (n) were obtained by Junpirom et al. [33].

4. Conclusion

Various techniques (XRD, XRF, TPO CHNS and TGA,) were used to define the coke formation and coke decomposition on six different catalysts. The low H/C mass ratio throughout the toluene alkylation with 1-heptene reaction indicated hydrogen-deficient coke. It was found that the structure of coke formed on H-mordenite and its modified samples is mainly amorphous carbon or polyaromatic coke with a high carbon content, while the structure of coke formed on H-beta and its modified samples is mainly non- or less-polyaromatic coke with a low carbon content, which points to the fact that the acidity of the catalyst used controls the type of coke accumulated during the reaction. The hypothesis of pore mouth catalysis is dominated by the type and amount of coke accumulated. The results obtained from the thermal decomposition process (i.e., TG and DTG profiles) indicate that there are two coke decomposition zones, the first for soft coke within the range of about 200 to 400 °C and the second for hard coke within the range of about 400 to 800 °C. H-beta parent and its modified samples show a maximum peak in the first zone at about 280 °C, which represent the high percent of soft coke. In contrast, H-mordenite parent and its modified samples display the biggest peak in the second zone at approximately 700 °C with the main decomposition of hard coke. Moreover, the overall values of activation energies for coke decomposition obtained with the parent H-mordenite and dealuminated H-beta zeolite catalysts are the highest compared to the other used catalysts, and thus, the conversion and selectivity of the desired product (i.e. 2-heptyl-methylbenzene) were higher on their surfaces compared to the rest of the catalysts because the rate of coke formation during the reaction time is slower. It was observed that at the reaction time of 360min, the conversions were 84.67% and 85.3% over dealuminated H-beta and H-mordenite, respectively, and this result was attributable to the reduction of the ratio of hard:soft coke accumulated during the time, as this ratio decreased only on the surface of these two catalysts compared to other catalysts, and this reinforces the role played by hypothesis of pore mouth catalysis.

Finally, by comparing the error obtained from this mathematical model, it was found that the reaction order model f(α)= (1- α)^n is most suitable for representing the decomposition of coke; therefore, this model was applied to simulate the results of thermogravimetric analysis.

Nomenclature

A	Frequency factors
$d\alpha/dt$	Degree of conversion
E_a	Activation energy (J/mol)
$f(\alpha)$	Reaction model
K	Reaction rate constant
m_a	actual weight
m_f	final weight
m_i	initial weight
N	Number of experiments
n	Reaction order
R	Ideal gas constant (J/mol. K)
R^2	Correlation Coefficient
T	Temperature (°C)
$y^{exp.}$	Experimental data
$y^{pred.}$	Predictable data

Greek letters

α	Conversion
β	Heating rate

CRediT authorship contribution statement

Ali Al-Shathr: Conceptualization. **Bashir Y. Al-Zaidi:** Data curation. **Amal K. Shehab:** Visualization, Investigation. **Zaidoon M. Shakoor:** Writing – original draft. **Safa Aal-Kaeb:** Software. **Laura Quintana Gomez:** Validation. **Hasan Sh. Majdi:** Supervision. **Emad N. Al-Shafei:** Methodology, Software. **Adnan A. AbdulRazak:** Writing – review & editing. **James McGregor:** Writing – review & editing.

Declaration of Competing Interest

None.

Data availability

Data will be made available on request.

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