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A novel thermogravimetric method for coke precursor characterisation

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Abstract

A novel thermogravimetric methodology is introduced to study the characterisation of coke precursors. The effect of different reactants, time on stream, and reaction temperature on coke precursor formation and chemical characterisation was investigated. This allowed us to classify coke precursors into "small" and "large" ones. Coke precursors are formed preferentially on the strongest acid sites at a rapid rate, with fast further transformation to other coke species. Furthermore, the method revealed a maximum of large coke precursors with time on stream due to their fast transformation into hard coke over strong acid sites compared with the much slower formation from small coke precursors over weak acid sites.

Keywords: HUSY zeolite; 1-Pentene; *n*-Heptane; Ethylbenzene; TGA; Coke

1. Introduction

During organic reactions catalysed by solid acidic catalysts, the catalyst always suffers from strong deactivation due to formation and retention of heavy byproducts, which cause poisoning and/or pore blockage of active sites [1]. The formation of these carbonaceous residues on hydrocarbon processing catalysts is of considerable technological and economic relevance to the oil and petrochemical industry [2]. These nondesorbed byproducts, called coke, consist of a mixture of high-molar mass, hydrogen-deficient, low-volatility components deposited on the solid catalyst.

Coke components can be classified into two kinds: coke precursors and hard coke [3]. Coke precursors are removed from the catalyst sample simply through volatilisation in inert nitrogen, whereas hard coke remains on the catalyst even at high temperature (873 K) and is removed by burning. Furthermore, coke precursors are chemically active. They are the prominent intermediates in the entire reaction network, and their adsorbed amount is comparable to that of fresh reactant [3].

In catalytic cracking, the behaviour of coke during the initial time on stream (TOS) is of great importance, because the amount of coke increases very rapidly while the catalyst activity decreases accordingly during this period [4]. The initial deactivating effect of coke is most pronounced during the reaction. Coke is formed from alkenes, alkanes, and aromatics produced during the cracking reaction through a sequence of reaction steps, including protonation, alkylation, isomerisation, hydride transfer, deprotonation, and ring closure, that result in the formation of large polyaromatic molecules [1]. The mass fraction of coke precursors increases rapidly in a short TOS. During this period, the amounts as well as the composition of coke precursors are more strongly affected by the reaction mechanism, reaction temperature, TOS, and sample handling procedures [5].

An in-depth understanding of the chemical character of coke precursors allows the further study of catalyst deactivation as well as the development of improved catalysts that generate less coke and are less sensitive to deactivation. Coke characterisation is often limited to determining its amount and bulk elemental composition. Some studies have been carried out on various aspects of coke character, including C/H ratio and composition [6–8]. One technique for identifying coke compounds, developed by Guisnet and co-workers [1,7,9], liberates coke from zeolite by dissolution of the framework in hydrofluoric acid and extraction by CH_2Cl_2. Coke components are recovered as soluble and insoluble coke. The soluble components can be determined using IR, UV–vis, and GC/MS. This characterisation technique is complex and time-consuming. There

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is an incentive to develop a simple, rapid method to provide some information about the coke precursor's character and, more specifically, its volatility.

The methodology presented here is based on determining how easily coke precursors are removed in an inert, nonoxidative atmosphere. The character of a coke precursor is evaluated based on its ability to be removed from the catalyst. At each temperature, coke precursors are either volatilised or decomposed to smaller fragments that escape from the catalyst. Current work is further examining the exact mechanism of coke precursor removal through TGA experiments with different heating rates for estimating the apparent activation energy of the process. Relatively high apparent activation energy values should indicate decomposition as a chemical activated process, whereas low values should indicate diffusion limitation, possibly through volatilisations. Furthermore, possible collaboration with a research group with access to GC/MS instruments could characterise the molecular composition of the coke components removed during the TGA thermal treatment.

Another feature of the method is that the results are expressed as fraction of the total amount of coke precursors at the corresponding conditions. Thus, comparisons at different conditions are independent of their total amount. This method was used to investigate coke precursor characterisation on UHSY zeolite during reactions of 1-pentene, *n*-heptane, and ethylbenzene. The effects of TOS and reaction temperature during 1-pentene cracking were also examined.

2. Experimental

2.1. Materials

The USHY zeolite catalyst was provided by Grace Gmbh in powder form with an average particle size of 1 μm, a framework Si/Al ratio of 5.7, and a bulk Si/Al ratio of 2.5. The micropore area was 532.4 m^2/g, and the micropore volume was 0.26 cm^3/g. BET surface area was 590 ± 23.5 m^2/g. The catalyst was pressed into pellets, crushed, and sieved, producing 1.0- to 1.7-mm particles as in previous studies [3,5]. Before each reaction, the catalyst was calcined in an oven at 873 K for 12 h. The 1-pentene (99% purity) and ethylbenzene (99% purity) were supplied by Sigma-Aldrich. *n*-Heptane (99.5% purity) was from BDH Chemicals Ltd. Nitrogen (CP grade) was provided by the BOC group as carrier gas.

2.2. Experimental procedure

Coking reactions with 1-pentene, *n*-heptane, and ethylbenzene as reactants were carried out on USHY zeolite at 523–623 K and atmospheric pressure in a stainless steel tubular fixed-bed reactor with an inner diameter of 15 mm. The amount of calcined catalyst used in each experiment was 0.65 g (1-cm-long catalyst bed). The carrier gas—nitrogen—was passed through a saturator containing the particular reactant placed in a heated water bath at a specified temperature (for 1-pentene, $P_{N_2} = 0.2$ bar, $P_{\text{reactant}} = 0.8$ bar; for *n*-heptane, $P_{N_2} = 0.65$ bar, $P_{\text{reactant}} = 0.35$ bar; for ethylbenzene, $P_{N_2} = 0.88$ bar, $P_{\text{reactant}} = 0.12$ bar) and then into the fixed-bed reactor. Unfortunately, achieving the exact same experimental conditions with all three reactants was not possible, due to the huge volatility difference of these components. After a specified TOS that denoted the end of the experimental run, the saturator was bypassed, and the reactor was allowed to cool for 10 min under nitrogen atmosphere. Then the reactor was disconnected from the rig and placed in ice for rapid cooling to ambient temperature. Coked samples were obtained at 1, 2, 3, 7, and 20 min of TOS and investigated by our novel method with a TGA apparatus (Cahn TG 131).

About 150 mg of coked sample was heated to 473 K at a rate of 10 K/min and maintained there for 60 min under flowing nitrogen (60 mL_N/min) to remove adsorbed water and reaction-mixture components. Then the temperature was raised to 873 K at a rate of 10 K/min and kept there for 30 min under nitrogen flow (60 mL_N/min). During this period, coke precursors were removed, decreasing the sample weight. The hard coke deposited on the catalyst was burnt off by switching from nitrogen to air at the final temperature (873 K) at the same flow rate; then its weight was measured. The amount of coke precursors in the catalyst was calculated as the difference between the sample mass after drying at 473 K and switching from nitrogen to air at 873 K. The amount of hard coke was estimated by the mass difference of the catalyst sample between before and after the switch from nitrogen to air, when the hard coke was completely burnt off [3]. The procedure of calculating coke precursors/hard coke is illustrated in Fig. 1.

3. TGA methodology for coke precursor characterisation

As shown by the original TGA curve (Fig. 1), the coke precursor contribution is from TGA running time $t = t_0$ to $t = t_0 + t_e$, with a TGA running temperature of 473–873 K, where t_0 ($t_0 = 80$ min) is the time at which removal of coke precursors starts, that is, when the TGA temperature begins to increase from $T_0 = 473$ K at a heating rate of 10 K/min and $t_0 + t_e$ ($t_e = 70$ min) is the time of the switch from nitrogen to air after the TGA temperature has remained at the final temperature (673 K) for 30 min. Furthermore, m_0 at $t = t_0$ (i.e., $T_0 = 473$ K) is the sample weight after removing adsorbed water and reaction-mixture components; m_e at $t = t_0 + t_e$, that is, after 30 min at $T = 873$ K, is the sample weight after removing coke precursors; and $m(t)$ is the sample weight at any time t, $t_0 \leqslant t \leqslant t_0 + t_e$. In the figures showing the TGA runs, $t_0 = 80$ min becomes time 0 and ($t_0 + t_e$) becomes 70 min.

The total mass of pure dry USHY zeolite is m_z. The total mass of coke precursors can be expressed as $m_{cp}^{tot} = m_0 - m_e$.

The mass of coke precursors that have been removed from coked catalyst at time t is $m_{cp}^{removed}(t) = m_0 - m(t)$. The mass of coke precursors that remain on the catalyst at time t is $m_{cp}^{remained}(t) = m(t) - m_e$. Thus, the total mass concentration of coke precursors in the catalyst (in g/g_{cat}) is

$$C_{cp}^{tot} = \frac{m_{cp}^{tot}}{m_z} = \frac{m_0 - m_e}{m_z}.$$

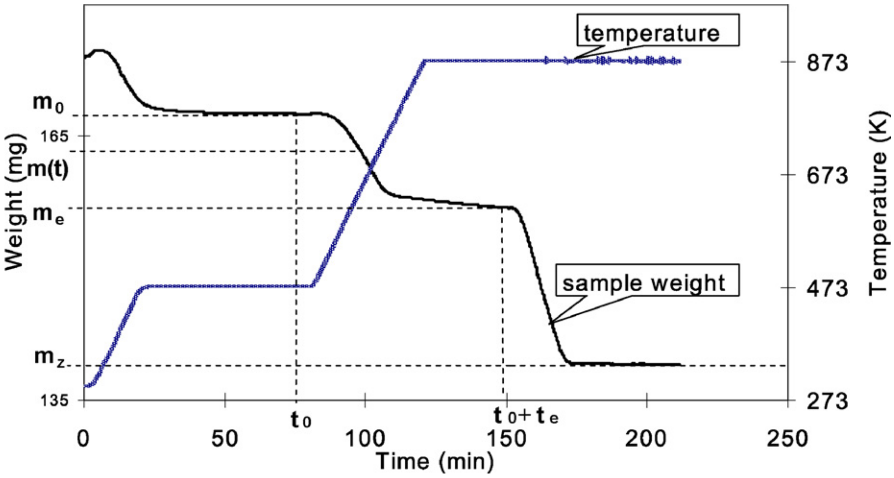


Fig. 1. Coke precursors and hard coke of a coked sample during thermogravimetric analysis.

The mass fraction of coke precursors removed from coked catalyst at any time t is

$$F_{\mathrm{cp}}^{\mathrm{removed}}(t)=\frac{m_{\mathrm{cp}}^{\mathrm{removed}}(t)}{m_{\mathrm{cp}}^{\mathrm{tot}}}=\frac{m_0-m(t)}{m_0-m_{\mathrm{e}}}.$$

The mass fraction of coke precursors remaining on the coked catalyst at any time is

$$F_{\mathrm{cp}}^{\mathrm{remained}}(t)=\frac{m_{\mathrm{cp}}^{\mathrm{remained}}(t)}{m_{\mathrm{cp}}^{\mathrm{tot}}}=\frac{m(t)-m_{\mathrm{e}}}{m_0-m_{\mathrm{e}}}.$$

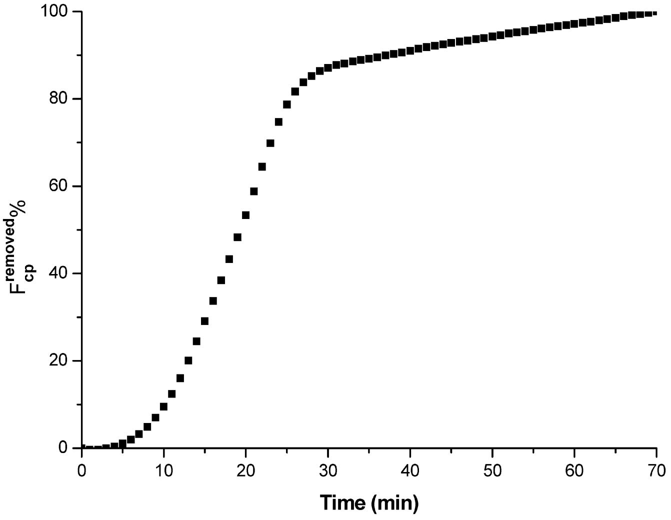
Fig. 2a shows the mass fraction of coke precursors removed from the coked catalyst running from 0 to 100% against TGA time of 0–70 min, that is, from t_0 to (t_0+t_{e}). Fig. 2b shows the mass fraction of coke precursors removed from the coked catalyst, running from 0 to 100%, against TGA temperature of 473–873 K.

Because the sample was maintained at 873 K for 30 min during the TGA run, it is not possible to differentiate weight loss during this final 30-min stage, which appears as a vertical jump at the final temperature. Obviously, complementary plots of $F_{\mathrm{cp}}^{\mathrm{removed}}$ versus temperature, as well as $F_{\mathrm{cp}}^{\mathrm{remained}}$ versus time, are possible as well. Throughout this paper, we present results in the form of $F_{\mathrm{cp}}^{\mathrm{removed}}$ versus time to also capture changes occurring during the last half hour at 873 K. Each graph also gives a temperature versus time plot to connect weight loss with temperature.

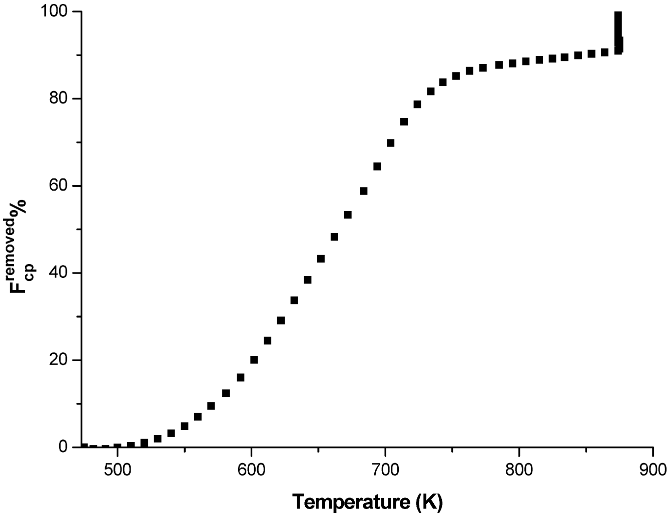
4. Results and discussion

4.1. Effect of different reactants

To investigate the application of this TGA method for coke precursor characterisation, we used different reactants: an alkane (n-heptane, 35% in N_2, residence time = 0.178 s, WHSV = 59.579 h^{-1}), an alkene (1-pentene, 80% in N_2, residence time = 0.055 s, WHSV = 86.211 h^{-1}), and an aromatic hydrocarbon (ethylbenzene, 12% in N_2, residence time = 0.239 s, WHSV = 25.886 h^{-1}). Unfortunately, achieving



(a)



(b)

Fig. 2. (a) Mass fraction of coke precursors removed from coked catalyst between t_0 and t_0+t_{e} against the TGA time. (b) Mass fraction of coke precursors removed on coked catalyst against the TGA temperature.

Table 1
Coke content of USHY zeolite coked during reactions of different reactants, $T = 623$ K, TOS = 20 min

$\% = g_{coke}/100\ g_{zeolite}$	Coke precursors (%)	Hard coke (%)	Total coke (%)
n-Heptane	1.74	0.78	2.52
Ethylbenzene	3.37	1.03	4.40
1-Pentene	5.73	15.40	21.13

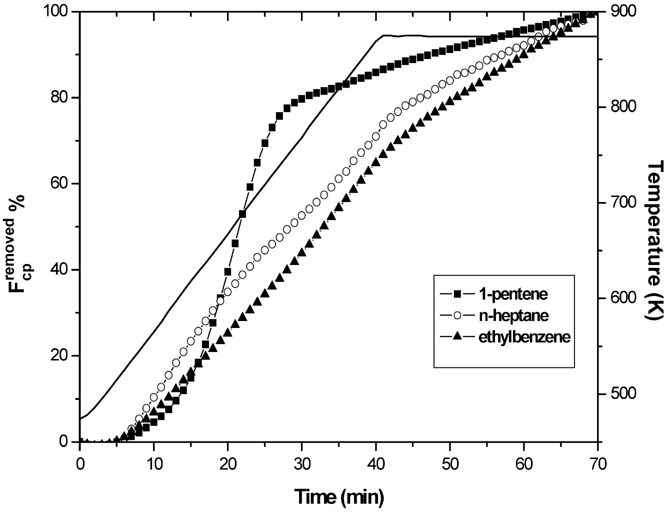


Fig. 3. Mass fraction of coke precursors removed from coked catalyst against the TGA running time for different reactants, reaction temperatures is 623 K, TOS = 20 min.

the exact same experimental conditions with all three reactants was not possible, due to the huge volatility differences among these components. The reaction temperature (623 K) and TOS (20 min) of the analysed sample were the same for all reactants, however. Different coking mechanisms occur with the three different reaction systems, resulting in different compositions of coke precursors [3,9] as well as different ratios of coke precursors to hard coke, as shown in Table 1.

Fig. 3 plots the mass fraction of coke precursors removed from the coked zeolite of these reactions against the TGA running time. We see that coke precursors in the *n*-heptane and ethylbenzene systems are removed at relatively the same rate during the entire TGA run, indicating a uniform distribution of coke precursors. With 1-pentene, however, several changes in the removal rate occur during the run. In the first 5–15 min, the removal rate of 1-pentene coke precursors is quite low. During this time, removal of the 1-pentene coke precursors is more difficult than removal of the paraffin/aromatic systems. The rate of removal increases rapidly between 15 min (620 K) and 25 min (720 K), then slows considerably at 25–30 min (720–770 K) until the end of the TGA run. This phenomenon becomes clearer by looking at another way of plotting the results. From the original Fig. 3, by differentiation, we can estimate and plot the coke precursor removal rate against time, as shown in Fig. 4. Here the 1-pentene coke precursors show a relatively high peak at around 22 min, followed by a plateau at a considerably lower level until the end of the TGA run. With both other systems, the rate is spread out uniformly at a much lower level. Figs. 3 and 4 indicate a considerable variation in the chemical character of coke precursors, as evident from the mode of their removal in an inert atmosphere.

1-Pentene cracking occurs according to a carbenium mechanism [10]. It easily forms a carbenium ion when it is adsorbed on a Brønsted proton. These carbenium ions can be transformed into coke precursors through bimolecular reactions, such as oligomerization, alkylation and hydrogen transfer [11]. From the 1-pentene curve in Fig. 3, the ability to remove coke precursors decreases at 25 min, indicating that either the composition of coke precursors is not uniform and/or the stability of coke precursors differs greatly. For the alkylbenzene reaction on solid acids, an aromatic ring easily forms a carbonium ion [12]. The reaction process involves formation of the alkylbenzenium ion, followed by dealkylation [13]. During this kind of reaction, polyaromatic coke precursors are formed by accumulation of fused and/or bridged aromatic rings. Their diffusion into the pores is slow due to the strong adsorption of these basic character molecules on the acid sites, which is smoother than that of alkene [11], resulting in almost linear removal of the coke precursors with time. The chemical character of coke precursors from n-heptane, a paraffin, is between that of 1-pentene and ethylbenzene. In both cases, coke formation occurs slowly from the monoaromatics and alkanes, the transformation of which into alkenes and polyaromatics is slow. The formation of these coke-making molecules is then the limiting step of coking [11].

4.2. *Effect of TOS*

Fig. 5 presents the mass fraction of coke precursors removed at various TOS from coked USHY zeolite during 1-pentene cracking (1-pentene, 80% in N_2, residence time = 0.066 s, WHSV = 86.211 h^{-1}) at 523 K. It can be clearly seen that coke precursors are removed rapidly in the first 25 min of TGA time (473–720 K, 0–25 min), followed by much slower removal (720–873 K, 25–70 min). For all samples, coke precursor removal slows considerably at around 25 min (720 K), indicating the existence of two coke precursor types. The first group contains coke precursors removed at the first stage of the TGA procedure (0–25 min). Judging from their removal rate and lower temperature, this group comprises coke precursors that are more easily removed than those of the latter group. We call these "small coke" precursors, in contrast to "large coke" precursors, which are removed after 25 min. During the entire TGA run, the order of the curves remains the same: $F_{cp}^{removed}$ (TOS = 20 min) > $F_{cp}^{removed}$ (TOS = 7 min) > $F_{cp}^{removed}$ (TOS = 3 min) > $F_{cp}^{removed}$ (TOS = 2 min) > $F_{cp}^{removed}$ (TOS = 1 min). The mass fraction ratio of small coke to large coke precursors increases with TOS, which is a counterintuitive finding. On the other hand, plotting the corresponding mass fractions (including the mass fraction of hard coke) with TOS (Fig. 6) shows a maximum in the large coke precursor curve, which is indicative of reaction schemes in series: reaction mixture components → small coke precursors → large coke precursors → hard coke. Fig. 6 clearly shows that the decreased amount of large coke precursors is accompanied by a significant increase of the amount of hard coke and a much slower increase in the

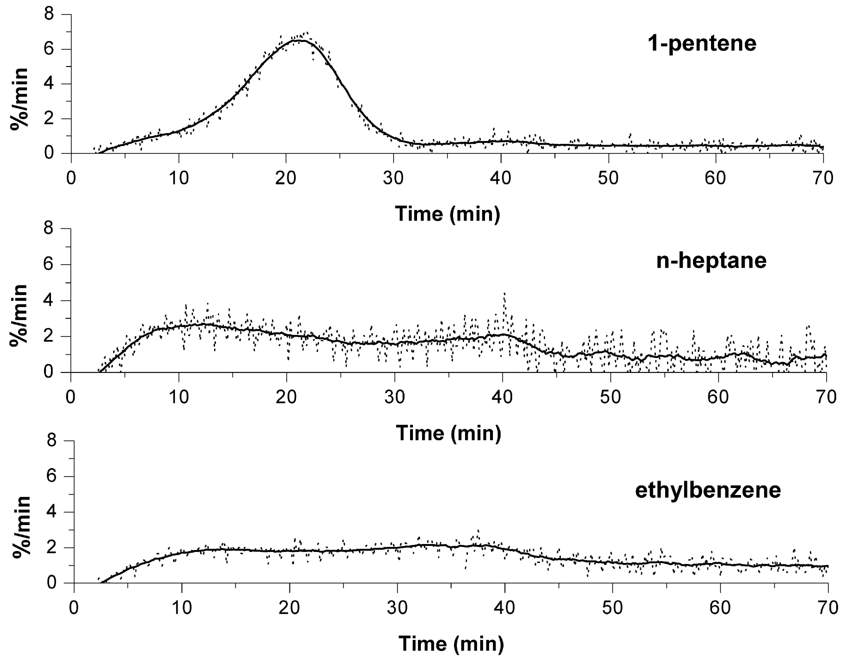


Fig. 4. Coke removal rate against TGA-time for samples coked during reactions of different reactants, 1-pentene, *n*-heptane and ethylbenzene. (Reaction temperature = 623 K, TOS = 20 min.)

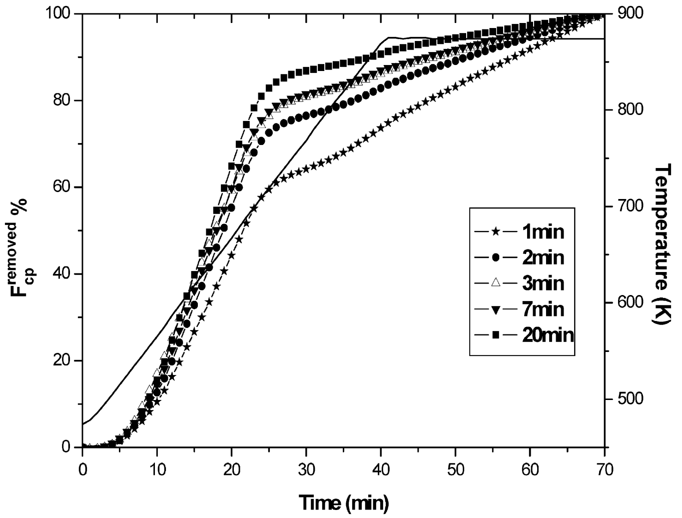


Fig. 5. Mass fraction of coke precursors removed from coked catalyst against the TGA running time at various TOS, reaction temperature = 523 K.

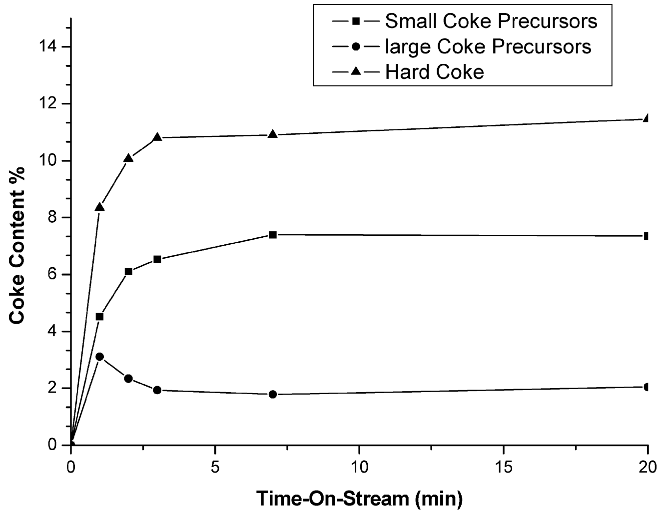
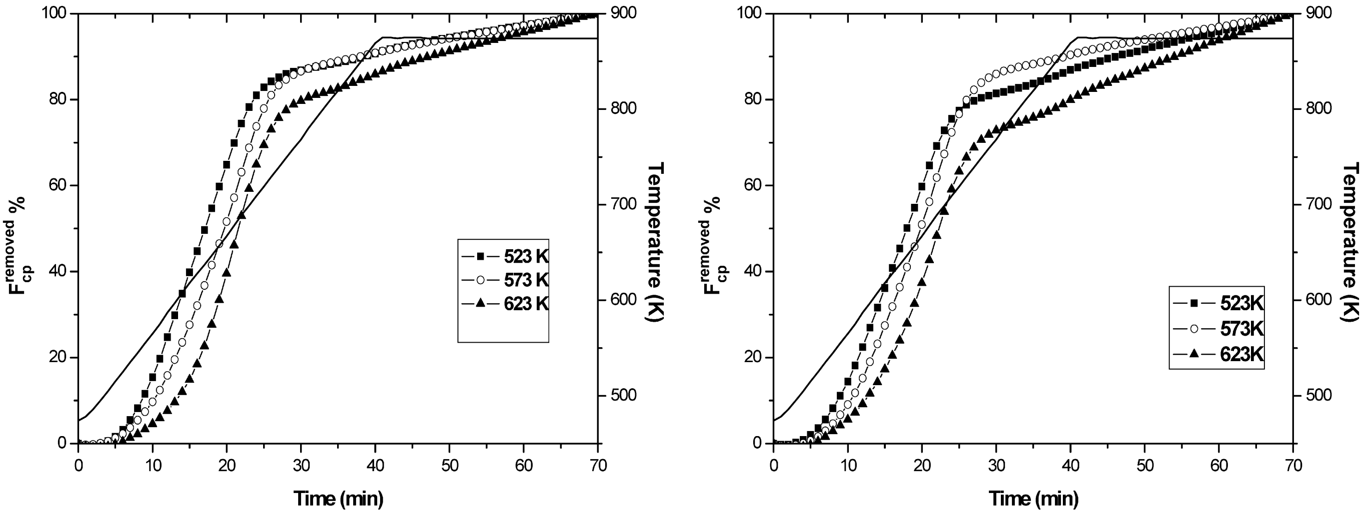


Fig. 6. Mass fraction of "small" and "large" coke precursors and hard coke at different TOS.

amount of small coke precursors. By itself, however, this reaction scheme does not explain the observed TOS run for the two coke precursor groups. The role of strong and weak acid sites must be taken into account.

During alkene reactions on USHY zeolite, the main reaction as well as coke formation occur first at strong active sites. At TOS = 1 min, GC analysis of the reaction mixture revealed considerably greater formation (in both number and size) of cracking/hydrogen transfer products than occurred later. Similar results have been reported previously [14,15]. With further increases in the number and size of coke precursors, they begin to be deposited on weak active sites, while the precursors on strong active sites grow larger. The results shown in Fig. 5 suggest that coke precursors deposited on strong active sites (i.e., at earlier TOS) are more stable than those formed on weak active sites. Soon all strong active sites are occupied by coke precursors. Thus, at longer TOS, a larger proportion of coke precursors on weak active sites are lighter. The rate of coke precursor removal is faster at later TOS compared with earlier TOS, because the fraction of coke compounds on strong active sites decreases with TOS. About 60% (TOS = 1 min) to 82% (TOS = 20 min) of coke precursors were removed in the weak active sites. The maximum mass fraction of large coke precursors is due to the rapid transformation of these precursors into hard coke over strong acid sites compared with the much slower formation from small coke precursors over weak acid sites.



(a) (b)

Fig. 7. (a) Mass fraction of coke precursors removed from coked catalyst against the TGA running time at various reaction temperatures, TOS = 20 min. (b) Mass fraction of coke precursors removed from coked catalyst against the TGA running time at various reaction temperatures, TOS = 3 min.

Coke is formed preferentially on the strongest active sites. Because these sites are the most active, the initial deactivating effect of coke is more pronounced than it would be if all of the active sites were of the same strength [16]. Through aromatization, coke deposits become larger and more aromatic with increasing TOS and coke content [2,9,17]. This is also demonstrated by the colour of the coked catalyst. The 20-min TOS sample is black, indicating strong aromatic character, whereas the 1-min sample is brown, indicating a less-unsaturated bond character. In the strong active sites of the coked sample at 20 min TOS, more coke precursors of greater stability were formed. In the weak active sites part, because of the long TOS, more coke precursors were formed as well. The most likely explanation for this phenomenon is that strong active sites are more deactivated for both 1-pentene cracking and coking. The reaction may be initiated at a few, very strong active sites, as suggested by the observed product distribution.

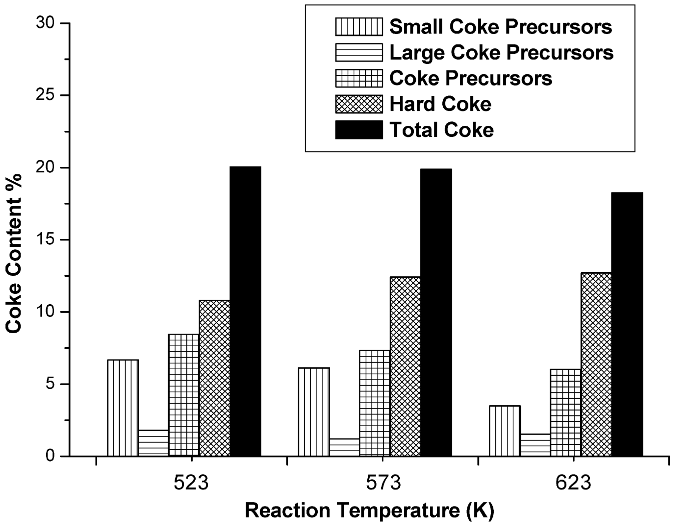


Fig. 8. Coke content at different reaction temperature (TOS = 3 min).

4.3. Effect of reaction temperature

Fig. 7 displays the mass fraction of coke precursors removed from coked catalysts at various reaction temperatures and two different TOS, 20 min (Fig. 7a) and 3 min (Fig. 7b), against the TGA running time. It is obvious that coke precursors from the sample of low reaction temperature are more easily removed than those from the sample of high reaction temperature. This can be explained by the higher desorption of coke precursors into the gas phase and/or faster transformation of coke precursors to hard coke with increasing reaction temperature [3]. Furthermore, coke precursors are more aromatic and stable at high reaction temperature than at low reaction temperature [11]. Fig. 8 plots all coke groups against reaction temperature for TOS = 3 min. Coke precursor content decreases with increasing reaction temperature, due mainly to the significant decrease of small coke precursors. Large coke precursors remain almost constant, indicating almost equal rates of formation from small coke precursors and rates of disappearance into hard coke. Hard coke exhibits the opposite tendency, increasing slightly with increasing temperature. The total coke content decreases slightly with increasing reaction temperature due to the slightly greater temperature dependence of coke precursors compared with hard coke. Because it is a reaction-activated process, transformation of coke precursors into hard coke is likely faster at high reaction temperature [7], confirming the above explanation.

At strong active sites (25–70 min, 720–873 K), the $F_{cp}^{removed}$ values are closer to one another at different reaction temperatures (523, 573, and 623 K) at TOS = 20 min (Fig. 6) than at TOS = 3 min (Fig. 7). This finding is in good agreement with the foregoing results; long TOS results in strong active site deactivation rather than weak active site deactivation. Consequently, from Figs. 6 and 7, $F_{cp}^{removed}$ versus time, some information on coking mechanism can be derived.

5. Conclusion

Here was have introduced a novel, simple TGA methodology to characterise coke precursors. The new method provides insight into the chemical character of coke precursor components in terms of the mode of their removal in an inert atmosphere and allows further classification of coke precursors into small coke and large coke precursors. Furthermore, it reveals a maximum in the mass fraction of large coke precursors with TOS due to their fast conversion to hard coke over strong acid sites compared with their much slower formation from small coke precursors over weak acid sites. In the examples presented here, the method clearly reveals differences in coke precursors formed by different reactants (i.e., paraffins, olefins, and aromatics), as well as different reaction temperatures and TOS.

Acknowledgments

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