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In situ thermogravimetric study of coke formation during catalytic cracking of normal hexane and 1-hexene over ultrastable Y zeolite

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Abstract

The in situ behaviour of n-hexane and 1-hexene over ultrastable Y zeolite was studied quantitatively using thermogravimetric equipment at low (323–423 K), middle (523–623 K), and high (623–773 K) temperatures. At low temperatures, adsorption is the absolute dominant cause of catalyst weight change when either n-hexane or 1-hexene come in contact with US-Y, whose amount decreases with temperature. At middle temperatures, adsorption is also the dominant cause of catalyst weight change in the case of n-hexane, with the adsorbed amount, however, about one order of magnitude lower than at low temperatures, while for 1-hexene, oligomerisation from the olefinic reactant becomes the dominant cause of catalyst weight change. At high temperatures, oligomerisation from the olefinic products of catalytic cracking becomes the dominant cause of catalyst weight change for both cases, n-hexane as well as 1-hexene, while the extent of coke formation increases with temperature.

Keywords: Coking; Coke precursors; Zeolites; TGA

1. Introduction

Catalytic cracking over zeolite-based catalysts is an important reaction in the refining and petrochemical industry, which suffers from strong coking. Coke is a mixture of heavy, low boiling point, high molar mass by-products that remain on the catalytic surface causing deactivation. Coke as a secondary product of catalytic cracking and the main cause of catalyst deactivation has received considerable research attention over the years [1,2]. The composition of coke is complex as is that of coke precursors, namely intermediate components on the catalytic surface, which undergo further reactions to form coke in its final form. Coke precursors obviously are more volatile at high reaction temperatures. Hence part of relatively low molecular weight coke precursors is desorbed without blocking the catalytic surface.

Fixed-bed reactors are laboratory reactors widely used in the research of the main reaction of catalytic cracking as well as coke formation. A sample of coked catalyst is obtained at different times on stream [3–6] and the amount of coke is estimated by weight loss during coke burning, usually using thermogravimetric analysis equipment (TGA) [6,7]. When the coked catalyst sample is recovered from a high-temperature reactor, it is necessary that the reactor cools down from reaction temperatures of usually 623–773 K. During this cooling period, the amount and composition of coke precursors change. Consequently coke data, especially coke amount, gained from a fixed-bed reactor do not represent the in situ value.

The behaviour of coke during the initial time on stream (TOS) is of great importance in the study of catalytic cracking, for the amount of coke increases fast while the catalyst activity decreases accordingly during this period. Coke is formed from alkenes produced during the cracking reaction through a sequence of reaction steps, like protonation, alkylation, isomerisation, hydride transfer, deprotonation, and ring closure, that result in the formation of large polyaromatic molecules [8]. The fraction of coke precursors in the overall coke components is much higher at short TOS. During this period the amounts as well as the composition of

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coke precursors are more strongerly affected by reaction temperature and sample handling procedures. TGA, employing an electrobalance, allows continuous monitoring of the weight of a sample and hence could be ideally used as a reactor for following coking.

In this work, TGA was used directly as a reactor in the reaction of catalytic cracking to study in situ coke formation. The catalyst sample weight was measured continuously while the rate of weight change was calculated by differentiation over time. The weight increase of the catalyst sample during the experimental run represents not only coke and coke precursor components formed on the catalytic structure but also adsorbed reaction mixture components. As adsorption of the hydrocarbon reactant is the first process that takes place with the subsequent conversion into volatile reaction products and coke/coke precursors, the shape of the weight curve and the estimated derivative curve is characteristic of the prevailing phenomenon, namely adsorption or coking.

The in situ behaviour of *n*-hexane and 1-hexene over ultrastable Y (US-Y) zeolite was studied quantitatively in the initial as well as later period of time on stream and at low (323–423 K), middle (523–623 K), and high (623–773 K) temperatures in order to identify different mechanisms of coke formation and the multiple role of coke precursors in catalytic cracking.

2. Experimental

2.1. Materials

The acidic US-Y zeolite catalyst was kindly provided by Grace Gmbh in powder form with an average particle size of 1 µm, an overall Si/Al ratio of 2.5, and a framework Si/Al ratio of 5.7. Its micropore area was 532.4 m^2/g and its micropore volume 0.26 cm^3/g. The measured BET surface area was $590 \pm 23.5\ m^2/g$. The catalyst was pressed into pellets, crushed, and sieved, producing particles with sizes in the range of 1.0–1.7 mm.

All hydrocarbon reactants, *n*-hexane and 1-hexene, were supplied by Sigma-Aldrich (99% purity). Nitrogen (99% purity) was used as carrier gas.

2.2. Experimental procedure

The experiments were performed at a temperature range of 323–773 K and atmospheric pressure in TGA equipment (Cahn TG131). The catalyst was placed in a basket, hanging in the middle of a quartz reactor tube. The inert gas nitrogen or the reactants, *n*-hexane or 1-hexene carried by nitrogen, were introduced into the bottom of the quartz tube, flowing upward and exiting the reactor about 20 cm above the catalyst basket.

Two streams of carrier gas were used in order to avoid condensation. One route passed through two saturators in series placed in a heated water bath containing the reactant and then mixed with another route of pure carrier gas. By adjusting the flow rates of the two streams maintaining the total flow rate of nitrogen at 60 ml_N/min, the reactant partial pressure in the feed could be varied.

When the catalyst was placed in the basket, nitrogen was used as drying gas at a flow rate of 60 ml_N/min. The reactor temperature was increased from ambient to 873 K at a rate of 10 K/min, in order for the catalyst to be calcined, and was maintained at this temperature for 1 h. After that, it decreased to the reaction temperature at a rate of 20 K/min, where it was maintained for another 30 min.

After this half-hour, the reactant was introduced into the reactor. The reaction temperature was maintained constant through the reaction time. In the rest of the paper we will refer to this period as the reaction period. At the end of the reaction period, pure nitrogen was introduced at constant reaction temperature for another 30 min continuously. We will refer to this period as isothermal desorption.

After this second half-hour, the reaction temperature was increased to 873 K at a rate of 10 K/min and remained at this temperature for a further 30 min. We will refer to this period as temperature-programmed desorption (TPD).

Finally after the third half-hour, air was flowing into the TGA at 60 ml_N/min, and 873 K for a further 30 min, in order for the formed coke to be burnt. After that, the TGA system was cooled down under flowing nitrogen.

3. Results and discussion

3.1. Low-temperature effect (323, 373, 423 K)

3.1.1. *n*-Hexane results

The amount and rate of the catalyst weight percentage change during the reaction period, isothermal desorption, and temperature-programmed desorption are presented in Figs. 1 and 2.

It can be observed that the catalyst weight increases rapidly initially in the reaction period for about 10 to 13 min and then levels out. Correspondingly, the rate of weight change shows a sharp and asymmetric peak at about 3 min, while later it becomes nearly zero. The rate value at the peak is over 2% at all temperatures, 323, 373, and 423 K. The rapid weight increase stops abruptly at about 10–13 min, corresponding to 15.8% at 323 K, 9.0% at 373 K, and 4.5% at 423 K, indicative of adsorption saturation with the level decreasing with temperature. The further weight change is about 0.5% at 323 K, 1.0% at 373 K, and 1.0% at 423 K until the end of the reaction period.

From the above quantitative data, it can be concluded that adsorption is the absolute dominant phenomenon when *n*-hexane comes into contact with US-Y at low temperatures. The adsorbed amount rapidly increases with a shape similar to adsorption breakthrough curves and approaches an equilibrium value, which decreases with temperature. The rate of adsorption has a sharp peak initially, and then it levels off at a value almost zero.

From Fig. 1 it is also obvious that large amounts are desorbed during isothermal desorption, with desorbed amounts increasing with temperature. Especially at temperatures over 373 K, the amount of n-hexane adsorbed on the catalyst reaches the same value of 3%. This behaviour can be explained by the result of temperature-programmed desorption. In Fig. 2, it can be seen that temperature-programmed desorption of n-hexane after reaction and isothermal desorption at 323 K has two main peaks at 369 and 435 K, which correspond to different adsorption sites of n-hexane on US-Y. Temperature-programmed desorption after 373 or 423 K just passes the first peak temperature but does not reach the second peak temperature. In other words, the adsorption at temperatures above 373 K is mainly taking place on the strong adsorption sites of US-Y and results in the same adsorbed amount.

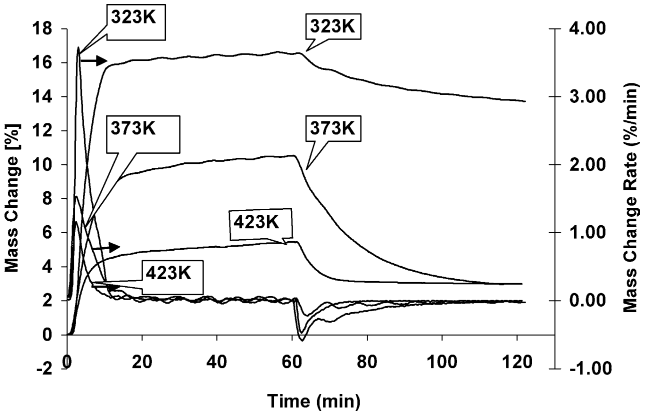

Fig. 1. Reaction period (60 min) and isothermal desorption of n-hexane at low temperatures (323, 373, 423 K). Nitrogen flow rate: 60 $\mathrm{ml_N}$/min. Partial pressure of n-hexane: 12.5 kPa.

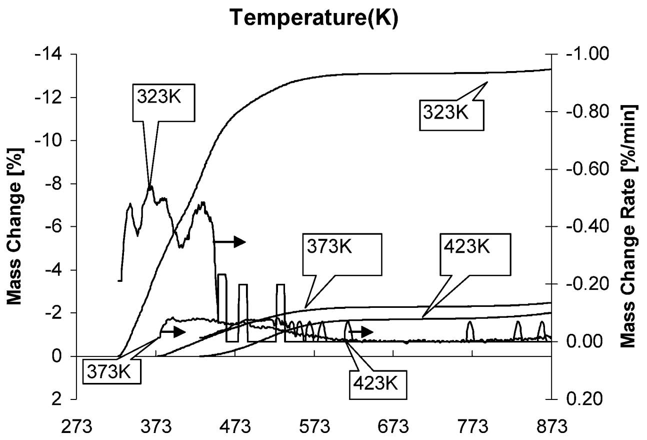

Fig. 2. Temperature-programmed desorption of n-hexane after reaction at low temperatures (323, 373, 423 K) with a heating rate of 5 K/min.

3.1.2. 1-Hexene results

The amount and the rate of weight percentage change of the catalyst sample in the reaction period, isothermal desorption, and temperature-programmed desorption are presented in Figs. 3 and 4. Similarly as with n-hexane, the amount of catalyst weight percentage change increases rapidly in the beginning of the reaction period for about 10 to 13 min. The rate of catalyst weight percentage change has a sharp and asymmetric peak at this initial time. In contrast to that with n-hexane, the amount at 323 K continues to increase at later times after the initial rapid increase, while transition at 423 K becomes more smooth. Accordingly, the rate at 323 K is maintained above zero, at 0.25%/min, during the rest of the experiment. The rate at 423 K decreases smoothly reaching a value of zero above 40 min.

The peak time for the rate is about 5 min and the amount of initial weight change is over 4%. An inflexion in the amount of curve at 323 and 373 K is observed at 10–13 min, while the amount of weight change is 20% at 323 K, continuously increasing to 28.0%, and 17.7% at 373 K. The inflexion in the amount of curve at 423 K is at 40 min, and the amount of weight change is 18.2%. The amount of weight change increases to about 12.0% at 323 K, 2.2% at 373 K, and 0.6% at 423 K later on.

From the above data, it can be seen that the adsorption is also the dominant phenomenon when 1-hexene comes into contact with US-Y at low temperatures, while the adsorbed

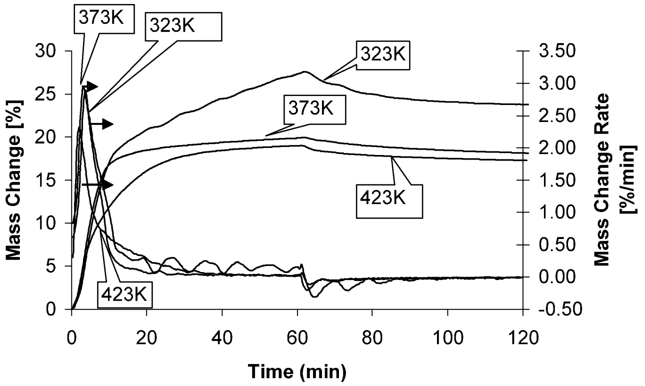

Fig. 3. Reaction period (60 min) and isothermal desorption of 1-hexene at low temperatures (323, 373, 423 K). Nitrogen flow rate: 60 $\mathrm{ml_N}$/min. Partial pressure of 1-hexene: 17.5 kPa.

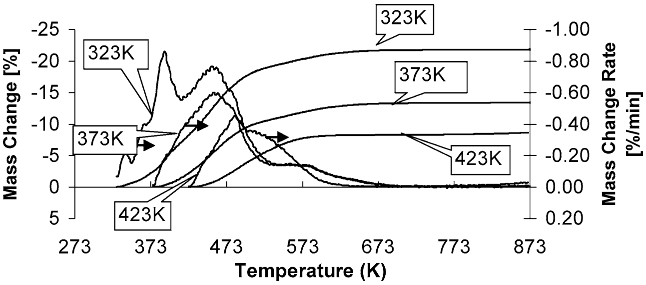

Fig. 4. Temperature-programmed desorption of 1-hexene after reaction at low temperatures (323, 373, 423 K) with a heating rate of 5 K/min.

amount increases. The rate has an initial sharp and asymmetric peak, especially at temperatures lower than 373 K, but other reactions obviously take place, contributing to formation of coke and/or coke precursors. We call the reaction taking place at 323 K “molecular clustering,” a low-degree oligomerisation reaction, to distinguish it from oligomerisation taking place at 423 K at a clearly higher degree. Significant coke formation reactions take place in a time scale comparable to that of adsorption. The low clustering at 323 K could be explained by the amount which continuously and steadily increases to 32% from a value of 20%, corresponding to a fast initial adsorption, while the rate is maintained at 0.25%/min. The oligomerisation at 423 K can also be explained by the distinct inflexion in the curve at temperatures lower than 373 K, which is in contrast to the smooth behaviour at 423 K.

In contrast to that with n-hexane, the amount desorbed during isothermal desorption is not noticeable at temperatures over 373 K. In Fig. 4, the temperature-programmed desorption of 1-hexene from the 323 K sample also has two main peaks at 394 and 462 K, similarly as with n-hexane, which correspond to different adsorption sites of 1-hexene on US-Y. The peak temperatures are higher than the corresponding ones with n-hexane due to stronger adsorption of 1-hexene compared to n-hexane on the same adsorption sites. Comparing the desorption curves from 323 and 373 K, there seems to be a striking similarity of the shapes above 373 K, indicating a similar composition of components adsorbed on the catalyst. This similarity is obvious in the adsorption curves (Fig. 3). The initial adsorption at 373 K, about 10–13 min, is the same as the adsorption at 323 K, but 1-hexene adsorbed at 373 K continues to react later on as well as during isothermal desorption for a similar product composition as that from 323 K. This is obvious in the considerably lower weight decrease of the 373 K sample during isothermal desorption than the 323 K sample. At 373 K the adsorbed 1-hexene is converted into coke/coke precursors rather than being desorbed. The temperature-programmed desorption from 423 K has only one peak and a relatively wide shoulder after that. The reason for the different peak shape compared with those at 323 and 373 K can be considered to be the product of oligomerisation under this temperature. The weight decrease of the 423 K sample during temperature-programmed desorption is a much lower fraction of the weight increase during the reaction period compared to the other two samples, indicating that the majority of the adsorbed amount has been oligomerised, leading to coke formation, rather than being desorbed.

3.2. Middle-temperature effect (523, 573, 623 K)

3.2.1. n-Hexane results

The amount and the rate of catalyst weight percentage change in the reaction period and isothermal desorption are presented in Fig. 5. Similarly as at low temperatures, the amount of catalyst weight increases rapidly initially in the reaction period for about 5–10 min. Correspondingly, the rate of catalyst weight change has a sharp and asymmetric peak at this time, leveling off later. Different than at low temperatures, the equilibrium value of the adsorbed amount descends at one order of magnitude. The peak time of the weight change rate is 2 to 3 min, and the amount of weight percentage change is only 0.2% at the same time. At 10–13 min there is an inflexion observed in the amount of curve, and the amount of weight change is 1.0% at 523 K, 0.9% at 573 K, and 0.3% at 623 K. The amount of weight change increases only at a further 0.4% at 523 K, 0.2% at 573 K, and 0.4% at 623 K.

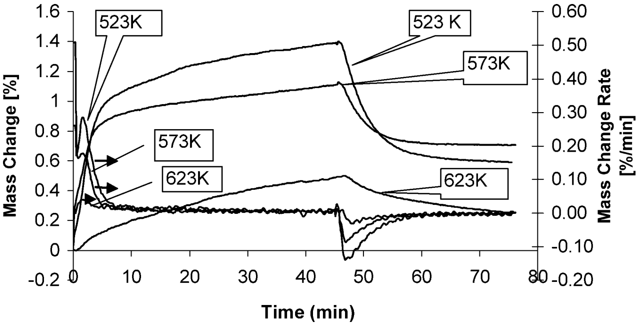

Fig. 5. Reaction period (45 min) and isothermal desorption of n-hexane at middle temperatures (523, 573, 623 K). Nitrogen flow rate: 60 ml_N/min. Partial pressure of n-hexane: 12.5 kPa.

It can be concluded that adsorption is also the dominant phenomenon when n-hexane comes into contact with US-Y at middle temperatures, a fact supported by the significant fraction of the adsorbed amount that is desorbed during isothermal desorption, as shown in Fig. 5. The shape of adsorption is the same as at low temperatures, i.e., initial rapid increase of the adsorbed amount approaching an equilibrium value that decreases with temperature, and the rate of adsorption has a sharp peak initially, while it is maintained at almost zero later. However, the adsorbed amount drops at about one order of magnitude.

The outstanding decrease of the adsorbed amount can be explained by the adsorption sites of n-hexane on US-Y. There are two main peaks at 369 and 435 K (Fig. 2) in temperature-programmed desorption of n-hexane from 323 K. Hence at reaction temperatures of 523 to 623 K, which are above both peak temperatures, the adsorbed amounts are very low.

3.2.2. 1-Hexene results

The amount and the rate of catalyst weight percentage change in the reaction period, isothermal desorption, and temperature-programmed desorption are presented in Figs. 6 and 7. Similarly as at low temperatures, the amount of catalyst weight percentage change during the reaction period initially increases fast for about 4 to 6 min, while the rate of weight change has a sharp and asymmetric peak at this initial time. The inflexion becomes smoother and, at later times,

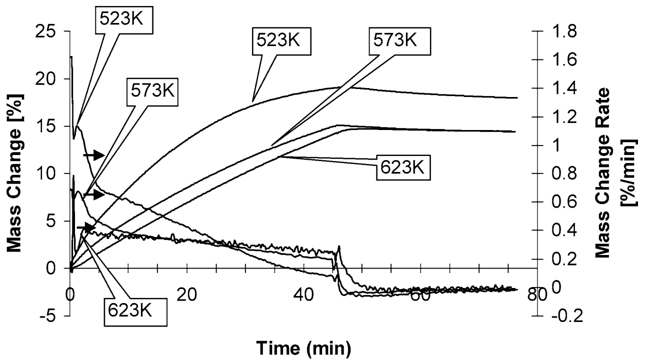

Fig. 6. Reaction period (45 min) and isothermal desorption of 1-hexene at middle temperatures (523, 573, 623 K). Nitrogen flow rate: 60 ml_N/min. Partial pressure of 1-hexene: 17.5 kPa.

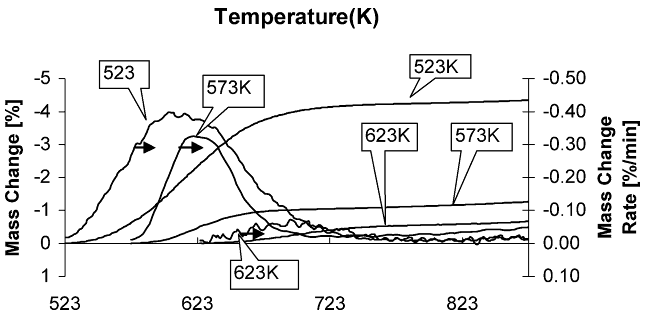

Fig. 7. Temperature-programmed desorption of 1-hexene after reaction at middle temperatures (523, 573, 623 K) with a heating rate of 5 K/min.

difficult to distinguish even at 623 K. Correspondingly the gradient of the rate decreases with temperature, while the rate is maintained above zero, even at 623 K, 0.26%/min.

It can be seen that adsorption does exist in a significant amount also at middle temperatures. The amount of adsorption increases fast and the rate of catalyst weight percentage change has a sharp and asymmetric peak initially, while the extent of adsorption decreases considerably with temperature. Oligomerisation becomes the dominant phenomenon during the whole reaction period; it even surpasses adsorption at 623 K at the beginning. The extent of oligomerisation also decreases with temperature. This can be seen by the change of the rate curve later on, while the rate of weight change at 623 K nearly levels off. Garwood reported the conversion of C_2–C_{10} alkenes on H-ZSM-5 zeolite in a vapour-phase process at temperatures of 473–533 K [9]. According to his results an alkene undergoes oligomerisation, isomerisation, cracking to a mixture of intermediate olefins that is independent of the nature of the feedstock, and copolymerisation to give a product spectrum with a wide distribution of carbon numbers. Pater et al. studied 1-hexene oligomerisation in liquid and vapour phases over USY zeolite catalyst under conditions of 473 K and 5 MPa, where they measured high oligomerisation selectivities in a range of 26–62% [10].

Similarly as with the isothermal desorption at low temperatures, the amount of isothermal desorption is not noticeable. The temperature-programmed desorption of 1-hexene from 523 and 573 K has one peak each at 613 and 626 K, respectively. Each one corresponds to the third peak shoulder at 573 K of temperature-programmed desorption from 323 and 373 K (Fig. 4)**,** which indicates the same component composition of coke. In conclusion, it is shown that oligomerisation is the dominating reaction in this temperature range.

3.3. High-temperature effect (673, 723, 773 K)

3.3.1. n-Hexane results

The amounts and the rate of catalyst weight percentage change in the reaction period and isothermal desorption are presented in Fig. 8. It can be seen that the behaviour of coke formation is obviously different from that at low and middle temperatures. First, the amount of coke at 673 K evidently is nearly one order of magnitude higher than at 623 K. It continues to increase during the whole reaction period, so that no breakthrough is observed in its curve, which would be characteristic if adsorption would have been the dominant phenomenon. Correspondingly, the rate of weight change decreases gradually from the beginning to the end of the reaction period. It is difficult to distinguish the sharp and asymmetric peak separating initial and later times. Secondly, the curve at 723 K is also different from that at 673 K, in the fact that the end amount increases with temperature. From the rate of weight change, it can be seen more clearly that the curve increases with time, which is also completely different from those at middle and low temperatures. Thirdly, the above tendencies of amount and rate become more pronounced as temperature increases; at 773 K the amount of coke increases to 23% at the end of reaction period and the curve becomes convex during the whole reaction time while a maximum rate value can be observed.

From the above data, the conclusion can be drawn that obviously the extent of coke formation increases with temperature. The curves of the amount and rate at 673 K are similar to those of 1-hexene at 623 K. This can be explained by the fact that coke is caused by olefinic products of *n*-hexane cracking and the coke formation is dominated

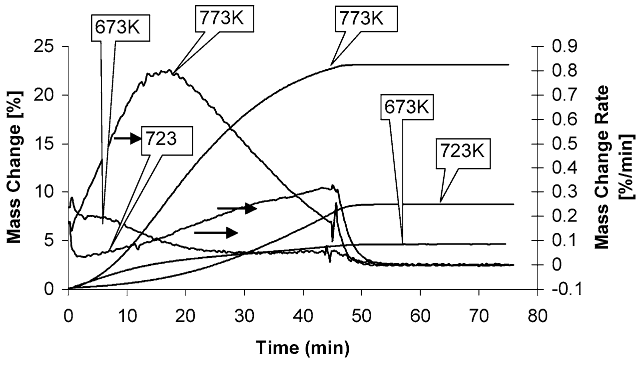

Fig. 8. Reaction period (45 min) and isothermal desorption of *n*-hexane at high temperatures (673, 723, 773 K). Nitrogen flow rate: 60 ml_N/min. Partial pressure of *n*-hexane: 12.5 kPa.

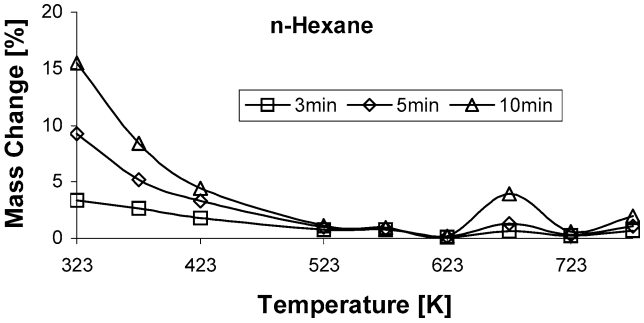

Fig. 9. Amount of catalyst weight change for n-hexane vs temperature at various TOS.

by direct oligomerisation, resulting in the same behaviour as 1-hexene at the lower temperature of 623 K. Different than at 673 K, an induction period of the coke formation initially and an acceleration period of rate later on are observed at 723 and 773 K. This indicates the existence of a different mechanism of coke formation at temperatures above 723 K.

Comparing the initial catalyst weight change rates at the same peak time of about 3 min at all three temperatures, it can be seen that they are similarly low as those at low and middle temperatures. Also the values of weight change at the same inflexion time of about 10 min are similar to those at low and middle temperatures. This tendency can be seen more clearly from Fig. 9, where the catalyst weight change is plotted against the temperature for different TOS: 3, 5, and 10 min. At low temperatures, the amount decreases with temperature and increases with TOS. The tendency is maintained at middle temperatures, the differences becoming, however, minute, while the overall values are one order of magnitude lower than at low temperatures. This tendency obviously changes at high temperatures, as cracking reactions become dominate and coke is formed by secondary reactions. Since adsorption is weaker at higher temperatures, however, and hence the amount of n-hexane adsorbed cannot be higher than that at middle temperatures, it can be deduced that the main cause of catalyst weight change becomes adsorption of products of n-hexane cracking, which include olefinic products as well as coke precursors and fully grown coke. This new tendency becomes clear at 673 K to highlight the different mechanism of cracking and coke formation.

It is usually accepted, based on data from a fixed-bed reactor, that the amount of coke initially increases rapidly reaching an inflexion point, followed by a slow increase to a maximum value. From the in situ data from TGA, however, it can be seen that there exists an induction and an autocatalytic acceleration period for the coke formation during catalytic cracking of n-hexane on US-Y at temperatures above 723 K.

3.3.2. 1-Hexene results

The amount and the rate of catalyst weight percentage change in the reaction period and isothermal desorption are presented in Fig. 10. It can be seen that in contrast to those at middle temperatures, at high temperatures the amount increases with temperature reaching 19.8% at 673 K and 22.4% at 723 K, compared to 14.6% at 623 K at the end of reaction. Regarding the rate of change, in contrast to previous tendencies of decreasing with TOS throughout the reaction period after the sharp initial increase, at high temperatures above 673 K the rate curve becomes convex, with this tendency being more pronounced at higher temperatures. The rate of coking at temperatures over 673 K resembles the shape of that of n-hexane at the even higher temperature of 773 K.

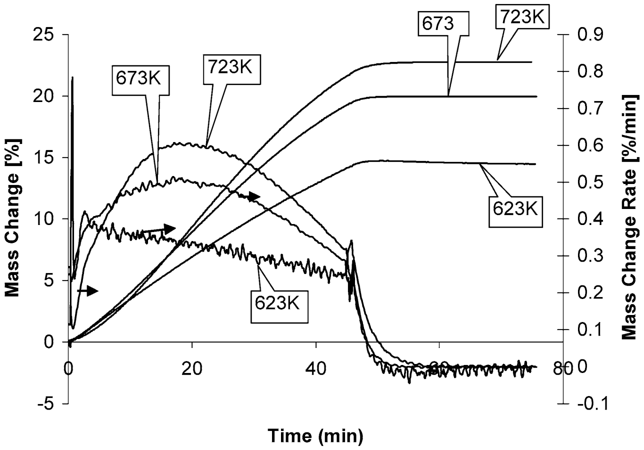

Fig. 10. Reaction period (45 min) and isothermal desorption of 1-hexene at high temperatures (673, 723, 773 K). Nitrogen flow rate: 60 ml_N/min. Partial pressure of 1-hexene: 17.5 kPa.

From these results, it can be concluded that, similar to the change of n-hexane from 673 K to 723 K, the mechanism of coke formation of 1-hexene alters from 673 to 723 K. The extent of direct reactant oligomerisation at a high-temperature range continues to decrease with temperature in a more pronounced form than at a middle-temperature range. It decreases significantly so that it cannot remain the main source of coke formation at the high-temperature range. Oligomerisation from the olefinic products of cracking becomes the dominant reaction leading to coke formation, which is also in competition with the cracking of coke precursors. Similarly as with n-hexane at 773 K, at temperatures above 673 K an initial induction period exists as well as an autocatalytic rate acceleration period later on.

While it can be said that coke formation from 1-hexene at temperatures above 673 K has the same mechanism as that from n-hexane at temperatures above 773 K, then n-hexane as paraffin and 1-hexene as olefin have a similar behaviour of coke formation during catalytic cracking at a high-temperature range. However, coke precursors produced by products of cracking have different functions at high temperatures than those of directly oligomerised intermediates from the olefin reactant at the middle-temperature range or oligomerised intermediates from olefinic products of n-hexane cracking at 723 K.

From Fig. 11 the tendency can be clearly seen that at low and middle temperatures, the amount decreases with temperature while it increases with TOS. The adsorption

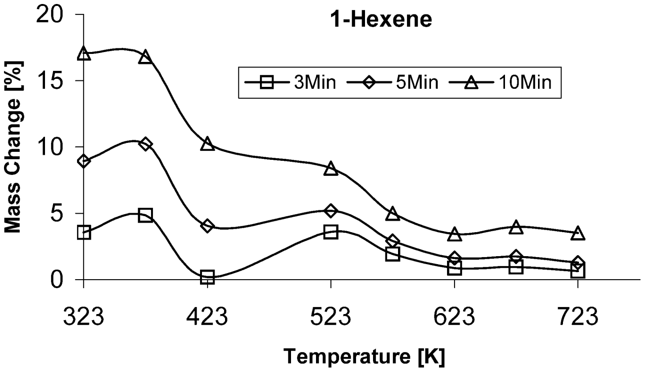

Fig. 11. Amount of catalyst weight change for 1-hexene vs temperature at various TOS.

and direct oligomerisation at low and middle temperatures both decrease with temperature. For the oligomerisation, the amount of coke formed by 1-hexene is maintained at one order of magnitude higher than n-hexane at middle temperatures. This tendency obviously changes at high temperatures, as the cracking reaction becomes the dominant reaction and coke is formed mainly by secondary reactions, replacing those of the direct oligomerisation from reactant and olefinic products. At temperatures over 673 K, the new tendency is much stronger. The induction and autocatalytic acceleration period present at temperatures over 673 K indicate the same mechanism of coke formation for both olefin and paraffin at the high-temperature range.

The same results have been observed by Reyniers et al. during cracking of isobutane over US-Y [11] and Figueiredo et al. from propylene on a commercial FCC-catalyst [12], which was explained by the fact that β-scission is favoured over oligomerisation at higher temperatures, and coke precursors are more volatile in nature and more easily desorbed from the catalyst than at lower temperatures.

In the oligomeric cracking mechanism introduced by Williams et al. [13], the oligomeric cracking scheme includes alkylation or oligomerisation reactions, in addition to the hydride-transfer/scission cycles of bimolecular cracking, with the key difference that the surface carbenium ion involved in the cycle may be significantly larger than the feed. This large surface carbenium ion was explained to be the coke precursors.

The induction period for the amount and autocatalytic period for the rate can be considered as an indication of the multiple role of coke precursors in diversity and competition/coexistence of catalytic reactive species on the surface of zeolite catalysts, both as intermediates of oligomerisation and intermediates of isomerisation and cracking reactions.

From the data of the amount of catalyst weight change at the initial period of both n-hexane and 1-hexene, it can be seen that the amount of coke at high temperatures is relatively low, lower even than 0.2% for n-hexane and 0.6% for 1-hexene at 3 min, which includes also the coke precursors. The actual amount of coke is much lower and cannot be compared with the adsorbed amount at low and middle temperatures. This low concentration of coke precursors on the catalyst surface at the initial period indicates the role of intermediates of catalytic cracking, which are continuously created by the olefinic products of either paraffin or olefin cracking or directly by an olefinic reactant. They take part in the cycle of catalytic cracking reaction, like the scission step and alkylation step (oligomerisation), at the same time. In the initial period of reaction, the amount of coke precursors is very low, with the result that their role is restrained compared with scission, leading into the induction period of coke formation. When the coke precursor amount increases to a certain extent, the extent of alkylation is strengthened, but this alkylation involves coke precursors existing on the catalyst surface. This is differently than with direct oligomerisation, which results in the autocatalytic period of coke formation. It is different with the coke formation with n-hexane as reactant at temperatures lower than 723 K and 1-hexene at temperatures lower than 673 K, which occur mainly by oligomerisation from the olefinic products of cracking or directly from olefinic reactant. This determines the behaviour of coke formation. The rate of coking gradually decreases all along the reaction, from the beginning to the end, as oligomerisation is only restrained by the diffusion of the olefinic reactant or decrease of olefinic products from cracking.

4. Conclusions

1. At low temperatures, 323–423 K, adsorption is the absolute dominant cause of catalyst weight change when either n-hexane or 1-hexene comes into contact with US-Y, whose amount decreases with temperature. For 1-hexene however, other causes obviously exist, like “molecular clustering” at 323 K and oligomerisation at temperatures over 373 K. n-Hexane from 323 K has two main peaks at 369 and 435 K on temperature-programmed desorption at 5 K/min, corresponding to different adsorption sites of n-hexane on US-Y. These peak temperatures shift to 394 and 462 K for 1-hexene due to stronger adsorption of 1-hexene than n-hexane on the same adsorption sites.

2. At middle temperatures, 523–623 K, adsorption is also the dominant cause of catalyst weight change when n-hexane contacts US-Y. The adsorbed amount, however, is about one order of magnitude lower than at low temperatures, which indicates that only a small proportion of active sites, no more than 0.2%, really take part in the catalytic cracking reaction at the beginning. For 1-hexene, oligomerisation from the olefinic reactant becomes the dominant cause of catalyst weight change; it even surpasses the initial adsorption at 623 K.

3. At high temperatures, 673–773 K, the induction and autocatalytic period present at temperatures over 673 K indicate the same mechanism of coke formation for both olefin and paraffin at this high-temperature range. Oligomerisation from the olefinic products of catalytic cracking becomes the

dominant cause of catalyst weight change and the extent of coke formation increases with temperature.

4. The induction and autocatalytic period for coke formation can be considered as the proof of the multiple role of coke precursors in diversity and competition/coexistence of catalytic reactive species on the surface of zeolite catalyst, both as intermediates of oligomerisation and intermediates of isomerisation and cracking reactions. The oligomeric cracking mechanism gains direct quantitative support from these coke formation phenomena.

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