Catalysis Letters Vol. 96, Nos. 3–4, July 2004 (© 2004)

Study of coke and coke precursors during catalytic cracking of *n*-hexane and 1-hexene over ultrastable Y zeolite

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Received 8 April 2004; accepted 30 April 2004

In this paper we report about coke formation during catalytic cracking of *n*-hexane and 1-hexene over acidic ultrastable Y zeolite in a fixed-bed reactor. The study is based on a classification between coke precursors, whose amount is estimated through volatilisation by nitrogen purging, and coke, large formed coke molecules that remain during nitrogen purging even at 873 K and whose amount is estimated by oxidation at that temperature. The role of coke precursors on the coking process and catalytic cracking reaction is discussed as well as differences in coking tendencies between the two reactants. The results show that the amount of coke precursors and/or coke may decrease with reaction temperature resulting into a reversal of the coking dependence upon temperature.

KEY WORDS: coke formation; thermogravimetric analysis; *n*-hexane; 1-hexene.

1. Introduction

Coke is a general name for a mixture of heavy, strongly adsorbed side-products formed on the surface of solid catalysts during organic heterogeneous catalytic reactions. It consists of a large number of non-volatile, low boiling point, low hydrogen content components and is usually the main cause of catalyst deactivation by poisoning active sites and/or blocking whole segments of catalyst pores.

Catalytic cracking over zeolite-based catalysts is an important reaction in the refining and petrochemical industry, which suffers from strong coking. Coke as secondary product of catalytic cracking and the main cause of catalyst deactivation has received considerable research attention over the years [1,2].

Albeit the advance in knowledge of coking and the introduction of advanced techniques for identifying these carbonaceous deposits, characterisation of coke remains the bottleneck in the elucidation of mechanisms of coke formation and hence development of new catalysts more resistant to coke formation and less sensitive to deactivation [3]. The determination of the amount and composition of coke on solid catalysts is of highest importance. The coke amount can be obtained by measuring the weight loss during coke burning. The coke composition on the other side can be identified by coke extraction after dissolution of the zeolite framework using HF [4]. Using the latter method, Guisnet *et al.* studied the effect of reaction temperature on coke composition. They classified and modelled two kinds of coke. At low temperatures, generally below 473 K, the formation of carbonaceous deposits involves mainly condensation and rearrangement reaction steps [3]. Therefore these deposits are generally non-polyaromatic and their composition depends strongly on the reactant. However, the composition of high temperature coke, above 623 K, is practically independent of the reactant. The coke components are generally polyaromatic in nature, hence their formation involves not only condensation and rearrangement steps but also various hydrogen transfer steps catalysed by acid sites [3].

The method to estimate the coke amount by weight loss during coke burning, usually using thermogravimetric analysis, also involves different heat treatments to remove water adsorbed in the course of obtaining the sample from the laboratory reactor, as well as adsorbed reactants and volatile products.

One estimation method considers only the weight loss by coke burning at high temperatures, ignoring the removal of any volatile light coke constituents [5]. The procedure involves heating of the coked catalyst sample taken from the laboratory reactor to 973 K at a rate of 10 K/min in an inert gas to remove any water adsorbed and/or reaction-mixture components. The only weight loss considered is at that final temperature when the gas switches to air.

Another method removes water at a comparatively low temperature of 473 K, which then increases to 1123 K at a rate of 10 K/min under flowing air. The amount of coke present in the zeolite is calculated by the total weight loss from the initial heat treatment at 473 K to the final catalyst sample at 1123 K [6]. During the period of increasing temperature volatile light coke molecules as well as heavy adsorbed coke molecules can

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either undergo cracking to yield smaller molecules which are desorbed or react *via* dehydrogenation leading to more condensed coke species. Coke components are chemically active and both, “light” and “heavy” coke change in character during thermogravimetric analysis. In this work we use the various steps of such an estimation procedure to discriminate between components of different chemical character, in order to provide using a simple procedure more quantitative information of coke formation not taken into consideration in previous work.

In this paper we report about coke formation during catalytic cracking of *n*-hexane and 1-hexene over acidic ultrastable Y zeolite (US-Y) in a fixed-bed reactor. The study is based on the above mentioned classification between coke precursors and coke, large formed coke molecules. The amount of coke precursors is estimated as the weight loss during volatilisation in a stream of inert nitrogen, while the amount of coke is estimated by burning of the remaining deposits. The role of coke precursors on the coking process and catalytic cracking reaction is discussed.

2. Experimental

2.1. Materials

The acidic US-Y zeolite catalyst was provided in powder form with an average particle size of 1 μm, an original 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 was 0.26 cm^3/g. The measured BET surface area was 590 ± 23.5 m^2/g. The catalyst was pressed into pellets, crushed, and sieved, producing particles with size in the range of 1.0–1.7 mm. Before each experiment, the catalyst was dried at 473 K for 2 h.

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

2.2. Experimental procedure

The experiments were performed at a temperature range of 523–723 K and atmospheric pressure in a stainless steel isothermal tubular fixed-bed reactor. The amount of dry catalyst used in each experiment was 1.0 g. 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, while maintaining the total flow rate of nitrogen at 60 mL_N/min, the reactant partial pressure in the feed was varied, taking the values 12.5, 17.5, and 22.5 kPa.

Upon completion of the experiment, nitrogen was flowing directly through the reactor for 1 h to ensure that any residual vapours throughout the system were discharged. Once the reactor had been cooled to ambient temperature, it was disconnected from the rig and opened to remove the catalyst.

The total catalyst sample was mixed and part of the coked catalyst, about 150 mg, was placed into a thermal gravimetric analysis (TGA) apparatus. The temperature of the TGA instrument was raised first to 473 K for 60 min under flowing nitrogen (60 mL_N/min) to remove adsorbed water and reaction-mixture components. A period of 60 min was found to be enough for this task, as the TGA weight indication stabilised during this time. Secondly, the temperature was increased to 873 K at a rate of 10 K/min and maintained there for 30 min under flowing nitrogen (60 mL_N/min). During this period coke precursor molecules were removed resulting into a sample weight decrease. This weight decrease started occurring immediately at the beginning of this phase, at 473 K, even with samples from reaction temperatures at 623 or 723 K. By switching from nitrogen to air at the same flow rate and at the final temperature (873 K), the coke deposited on the catalyst was burnt out and its weight measured.

The amount of coke precursors present in the zeolite was calculated by the difference between the initial catalyst sample mass after drying at 473 K and the sample mass just before switching from nitrogen to air at 873 K. The amount of coke present in the zeolite was calculated by the mass difference of the catalyst sample between before and after switching from nitrogen to air, when coke was completely burnt off. The total coke includes coke precursors and coke. The graph of coke weight of a catalyst sample in TGA and calculation of coke precursor and coke is shown in figure 1. All coke concentrations, expressed in percent, were estimated by dividing the corresponding coke amounts by the mass of

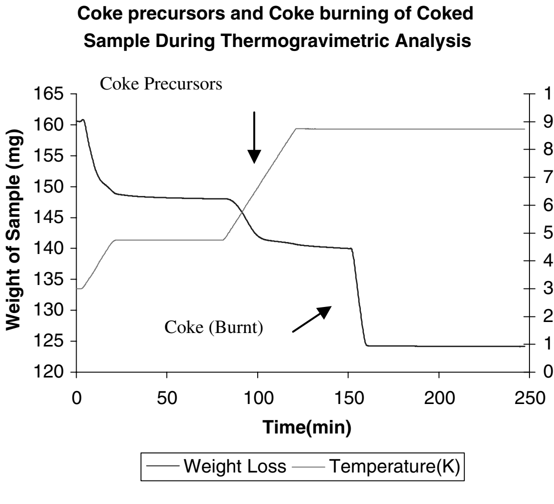


Figure 1. Coke precursors and coke of a coked sample during thermogravimetric analysis.

catalyst, which corresponds to the sample mass at the end of the TGA procedure after the burning of coke.

3. Results and discussion

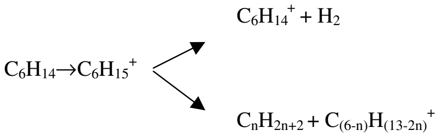
3.1. Temperature effect

3.1.1. n-hexane results

The amounts of coke precursors and coke produced during *n*-hexane reactions are presented in figure 2. The nitrogen flow rate was 60 mL_N/min, the partial pressure of reactant was 22.5 kPa and the total time-on-stream was 30 min.

It can be clearly observed that the amount of coke increases with reaction temperature being near zero at 523 K, while the amount of coke precursors has a maximum at 623 K. At 723 K it decreases, at a value even lower than at 523 K. Having a relatively low reactivity, normal hexane generally forms very low amount of coke at 523 K. This can also be confirmed directly by comparing the colour of the coked catalyst, light brown colour at 523 K and purple at 723 K. This is easy to understand as the catalytic cracking reaction depends strongly on temperature. The reason why it produces more coke precursors at lower temperature than at higher temperature is the following.

n-hexane as paraffin cracks according to monomolecular and bimolecular cracking mechanisms. The monomolecular cracking can be observed on low *n*-hexane partial pressure [7]. *n*-Hexane is protonated by Bronsted acid sites to form a carbonium ion. A shorter paraffin or hydrogen and a carbenium ion are produced when the carbonium ion is cracked or dehydrogenated.



$$C_6H_{14} \rightarrow C_6H_{15}^+ \begin{array}{l} \nearrow C_6H_{14}^+ + H_2 \\ \searrow C_nH_{2n+2} + C_{(6-n)}H_{(13-2n)}^+ \end{array}$$

The adsorbed carbenium ion can either be desorbed as an olefin or start the bimolecular cracking mechanism. The bimolecular cracking mechanism involves hydride-transfer to the surface carbenium ions from the paraffin reactant, and β-scission of the generated carbenium ion. Carbenium ions can also rearrange to get skeletal isomers. The reaction rates occurring in the bimolecular mechanism are much higher, especially at high reaction temperatures [8]. Coke is formed from the alkenes produced in the cracking reactions and proceeds through a sequence of reaction steps, i.e. protonation, alkylation, isomerisation, hydride-transfer, deprotonation and ring closure, finally leading to the formation of large polyaromatic molecules [9].

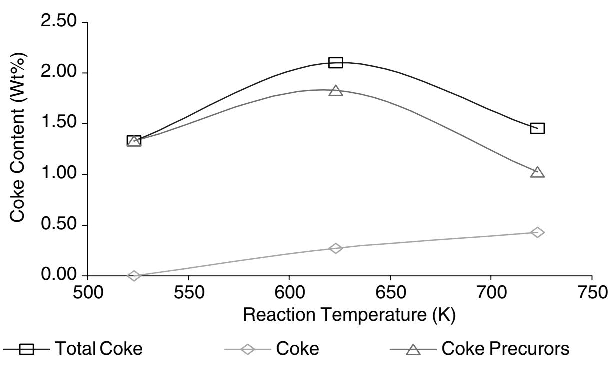


Figure 2. Coke content after 30 min time-on-stream of *n*-hexane cracking over US-Y at different reaction temperatures.

On previous work, similar results had been obtained [6]. At low reactant feed compositions (5% and 10%), the coke content decreased with temperature for both isooctane and 1-octene, explained by the higher desorption of the olefinic coke precursors into the gas phase with increasing reaction temperature that were responsible for coke formation. Coke precursors are obviously more volatile at high reaction temperatures. Consequently at 723 K, part of relatively low molecular weight coke precursors desorbs without being transformed into "harder" coke form, which is characterised as coke in our study. When reaction temperature decreases to ambient conditions, the amount and content of coke precursors also change. The data of coke precursors and coke from a fixed-bed reactor is not the exact result of coke amount formed *in situ*. They have been affected by the reaction conditions and sample handling. The fixed-bed reactor has to be cooled down after the experimental run with cooling periods varying according to reaction temperature. During this cooling period structural coke changes take place. This can also be seen at the results of solvent extraction of coke precursors using dichloromethane. The amount of dissolved coke precursors by dichloromethane at 523 K was 1.06%, most of it monoaromatic compounds. Coke precursors at 823 K could not be dissolved by dichloromethane suggesting that they were mostly polyaromatic compounds.

3.1.2. 1-Hexene results

The amounts of coke precursors and coke produced during 1-hexene reactions are presented in figure 3. The nitrogen flow rate was 60 mL_N/min, the partial pressure of reactant 1-hexene was 12.5/17.5 and 22.5 kPa, respectively.

1-Hexene as reactant forms nearly an order of magnitude more coke than *n*-hexane, which is indicative of the different mechanisms of catalytic cracking and coke formation by olefins and paraffins. Differently than by *n*-hexane cracking, the amount of coke precursors and coke both decrease with reaction temperature as shown in figure 3.

1-Hexene as olefin cracks according to carbenium mechanism [10]. It can directly and easily form a carbenium ion when it is adsorbed on a Brønsted proton. This carbenium ion can be isomerised, oligomerised and/or cracked. Once initiated, this pathway

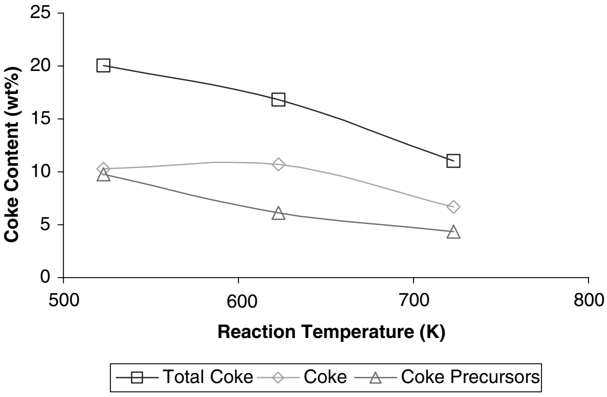


Figure 3. Coke content after 15 min time-on-stream of 1-hexene cracking over US-Y at different reaction temperatures.

may be up to 800 times faster, with much lower activation energy, than the monomolecular reaction [11]. It is favoured therefore at lower temperatures, higher partial pressures of alkene where higher carbenium ion coverage is obtained, or higher conversions [12].

Even at low temperature, coke can be formed directly through oligomerisation of the 1-hexene reactant, rather than cracking products, which are needed in the case of paraffin cracking. Oligomerisation is followed by cyclisation of the oligomers, transformation through hydrogen transfer into monoaromatics, alkylation of these monoaromatics, then cyclisation and hydrogen transfer to give polyaromatic components through aromatic ring fusion reactions [13]. Hence, the amount of coke in 1-hexene cracking is much higher than *n*-hexane at every reaction temperature level. But as the reaction temperature increases, the extent of oligomerisation reactions decreases, while cracking reactions are enhanced even exceeding oligomerisation above certain temperature. Coke precursors and coke produced from secondary cracking reactions become the main pathway of coke formation while the amounts of both, coke precursors and coke, decrease with temperature. At the same time, similarly to *n*-hexane results part of low molecular weight coke precursors desorbs without being transformed into coke. When reaction temperature decreases to ambient conditions, the amount and content of coke precursors also change.

3.2. The effect of partial pressure of reactant and TOS

To exclude the effect of different reaction temperatures and operation procedures on coke precursors and coke formation in a fixed-bed reactor, as well as to have the distinctive results of coke precursors and coke in catalytic cracking reactions, 1-hexene was selected as reactant to obtain data of coke in catalytic cracking at initial stages, 0–15 min time on stream, and mild reaction temperature, 523 K. The results are shown in figures 4–6, for coke precursors, coke and total coke, respectively.

From these figures, it can be seen that the amounts of both coke precursors and coke increase with TOS. Especially at the first 5 min, coke increases fast, from 0.4% at 1 min to 3.4% (12.5 kPa, 1-hexene) and from 1.6% to 6.2% (22.5 kPa, 1-hexene) at 5 min. The effect of partial pressure is not so obvious as this of TOS. Coke clearly increases with partial pressure at different TOS, but for coke precursors, at 1–5 min, the amount is nearly the same at different partial pressures. The increase of coke precursors is comparable with that of coke between 5 and 15 min, but it is higher at the first minutes, nearly 2%.

For 1-hexene catalytic cracking on US-Y catalyst in the initial 0–15 min, coke presursors are formed both from direct oligomerisation of 1-hexene as reactant and oligomerisation of the olefinic products of 1-hexene cracking. These precursors are further transformed *via* cyclisation of the oligomers, hydrogen transfer into monoaromatics, alkylation of these monoaromatics, as well as cyclisation and hydrogen transfer to give aromatics with double or triple fused rings resulting in the formation of large polyaromatic molecules, i.e. coke [3,4]. So both coke precursors and coke are formed increasingly as secondary products with TOS. The partial pressure of reactant is expected to have a positive effect to coke precursors, even if not obvious in the first 0–5 min of our experiments. This may be explained by a strong pseudo-zeroth-order initial coking on strong

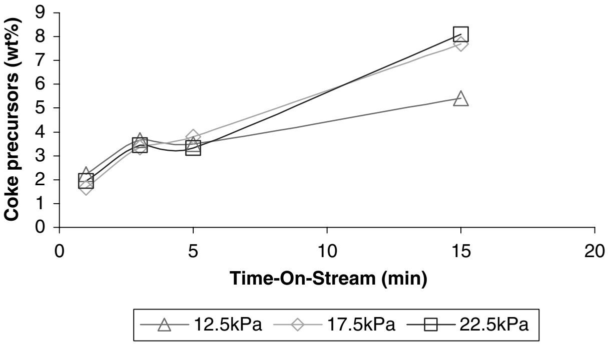


Figure 4. Coke precursors content during 1-hexene cracking over US-Y at different partial pressures of 1-hexene.

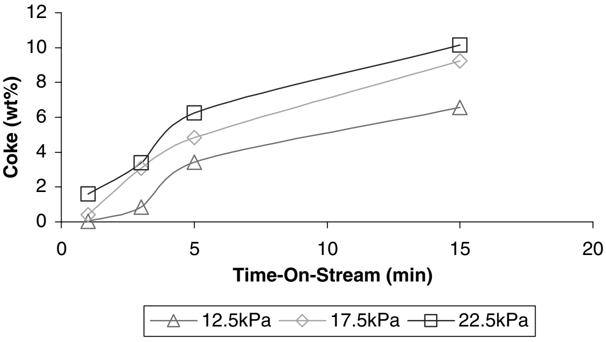


Figure 5. Coke content during 1-hexene cracking over US-Y at different partial pressures of 1-hexene.

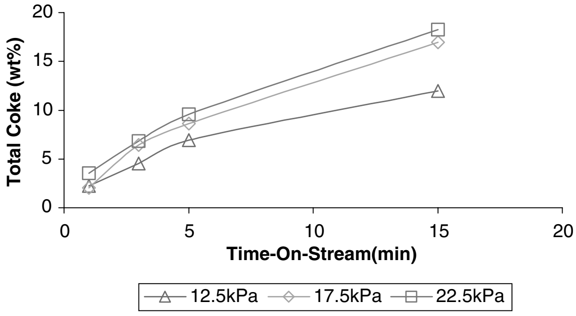


Figure 6. Total coke content during 1-hexene cracking over US-Y at different partial pressures of 1-hexene.

acidic sites [6], originated by a high coking kinetic constant relative to the concentration differences. This is possibly exaggerated by diffusion limitation that translated gas phase concentration differences into even smaller differences in surface coverage.

In order to highlight the importance of coke precursors and coke, we plotted the coke content of each group, coke precursors/coke/total coke, as fraction of the cumulative reactant mass fed into the reactor (figure 7) as well as fraction of the reactant mass fed into the reactor in one time unit, 1 min (figure 8). The latter is the coke amount divided by the reactant feed mass flow rate, which remained constant throughout the experiment. In the first plot, figure 7, the coke precursors curve decreases with TOS indicating a decrease of their formation rate. In the second plot, figure 8, the decrease of the formation rate is indicated by the decrease of the gradient of the curve. The corresponding coke curves show a maximum in their amount, figure 7, or their gradient, figure 8, at about 3 min. Until that TOS the amount of coke precursors is higher than this of coke, while after about 3 min this picture reverses. The initially formed coke precursors transform through surface reactions into large coke molecules, contributing this way also into the gaseous products formed by cracking reactions of coke precursors. Cracking of coke precursors in particular can explain gaseous products larger than the feed hydrocarbon molecule.

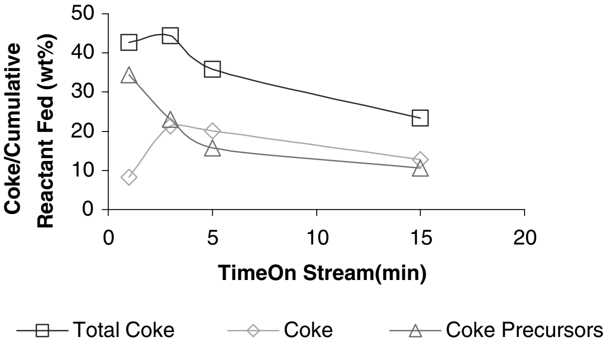


Figure 7. Coke content with time-on-stream as fraction of cumulative reactant during 1-hexene cracking over US-Y (partial pressure of 1-hexene: 17.5 kPa).

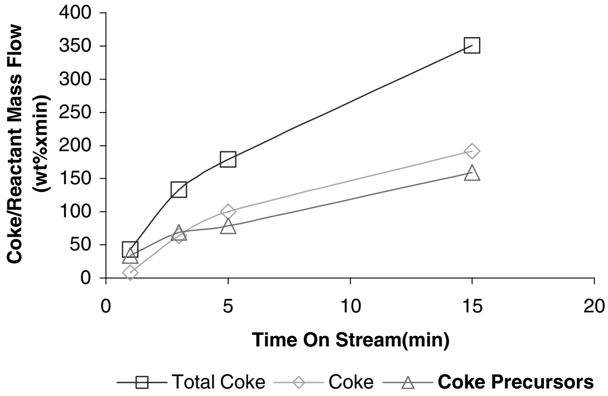


Figure 8. Coke content with time-on-stream as fraction of instantaneous reactant during 1-hexene cracking over US-Y (partial pressure of 1-hexene: 17.5 kPa). See text for explanation of term: instantaneous reactant.

Recently, Kung *et al.* introduced a new distinct mechanism as a refinement to the above classification of monomolecular and bimolecular cracking mechanism [14]. It is dominated by oligomeric cracking to explicitly account for the appearance of coke and for the formation of products larger in carbon number than the feed molecule.

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.

The large carbenium ion produced by alkylation or oligomerisation can be considered as active coke precursor adsorbed on the surface acidic sites. Similarly to 1-hexene cracking, high alkene partial pressures and high surface carbenium ion concentrations favour the alkylation or oligomerisation and form more coke precursors. The coke precursors, which may be alkanes or alkenes formed in the H-transfer reaction, may remain adsorbed on the surface because of their high molecular weight and undergo further H-transfer reactions with other carbenium ions of any size.

Additionally, the larger the molecular weight of an oligomeric carbenium ion the stronger its interaction with the zeolite. Hence its desorption as an alkene to terminate the chain reaction is less likely than for smaller carbenium ions in bimolecular cracking.

Coke precursors continuously grow larger when the alkylation step is faster than the scission step, causing the size of the surface oligomers to continue to grow and eventually cyclise to form aromatic coke. It can be expected that for US-Y, the cyclisation process is relatively slow with respect to H-transfer, so that the transient oligomeric carbenium ion can catalyse the conversion of many feed molecules before it forms an inactive coke molecule.

In conclusion coke precursors are the main products of 1-hexene catalytic cracking on US-Y catalyst in the initial 5 min on stream. They continue to form in significant amounts at the 5–15 min period but are converted mainly into cracking gaseous products rather than large coke molecules contained in "coke". Therefore coke precursors are the prominent intermediates in the overall reaction and must be considered in the catalytic cracking reaction, where they contribute into gaseous product formation.

4. Conclusions

We introduced a new methodology of estimating the amount of coke. In this, the total amount of coke molecules is classified into coke precursors, which are removed from the catalyst sample simply through volatilisation in inert nitrogen, and coke, which remains on the catalyst even at high temperature (873 K) and is removed by burning.

Coke precursors have higher volatility at high reaction temperatures, so that part of low molecular weight coke precursors desorbs and can not stick on the catalyst as *n*-hexane undergoes cracking on US-Y zeolite. As the reaction temperature decreases to ambient conditions, the amount and content of coke precursors also change.

The amount of coke in 1-hexene cracking is far more than *n*-hexane at every reaction temperature level, which shows the different catalytic cracking mechanism between paraffin and olefin. With the reaction temperature increasing, coke precursors and coke produced from secondary reactions of cracking products become the main path of coke formation, and their amounts both decrease.

Coke precursors are main products of 1-hexene catalytic cracking on US-Y catalyst in the initial 5 min, as well as they keep a high proportion in later times-on-stream, 5–15 min, contributing into gaseous product formation.

Coke precursors are the prominent intermediates in the whole reaction. They are chemically active and their adsorbed amount is comparable to this of the fresh reactant. They play an important function in the diversity, competition and coexistence of catalytic reactions on the surface of zeolites, such as isomerisation, oligomerisation and cracking.

Acknowledgments

SC thanks China Scholarship Council for one year State Scholarship Fund Award, Sinopec Beijing Research Institute of Chemical Industry for a leave of absence during this period and UCL for a Visiting Senior Research Fellowship at the Department of Chemical Engineering.

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