Chemical Engineering Journal 142 (2008) 217–223

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Deactivation studies during 1-pentene reactions over HUSY zeolite

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ARTICLE INFO

Article history:
Received 1 November 2007
Received in revised form 22 February 2008
Accepted 25 February 2008

Keywords:
1-Pentene
Coke
Deactivation
HUSY zeolite
Cracking
Isomerisation
TGA
Hard coke
Coke precursors

ABSTRACT

In this paper we report about catalyst deactivation during reactions of 1-pentene over acidic ultrastable Y zeolite in a fixed-bed reactor. The effects of reaction temperature and time-on-stream (TOS) on product distribution, conversion and coke formation are discussed. At this work various coke groups – coke precursors, hard coke as well as total coke amount – were followed with TOS. Furthermore, the effects of coking on 1-pentene reactions were also studied. Cracking and hydride transfer were the predominant reactions in the first minute of TOS which deactivated rapidly allowing isomerisation to become the main reaction afterwards. A steep increase of the amount of coke formed was observed initially which was in good correlation with the initial rapid deactivation. The hydrogen freed during this initial time from the formation of high a carbon-to-hydrogen (C/H) ratio coke components contributed to the formation of hydride transfer products.

1. Introduction

Acidic zeolites are an important group of solid catalysts for hydrocarbon reactions in the refining and petrochemical industry [1]. The most prominent example is the fluid catalytic cracking refinery process whose catalyst's active ingredient is ultrastable Y zeolite (USY). A variety of primary, secondary and tertiary products are formed during this reaction [2], generally accepted to proceed through the carbenium mechanism [3–7].

Hydrocarbon reactions over acidic zeolite catalysts are accompanied by the formation of coke which causes catalyst deactivation and changes in product distribution [8–12]. The initial deactivating effect of coke is most pronounced during hydrocarbon reactions over solid acidic catalysts. The amount of coke increases rapidly while the catalyst activity decreases accordingly during this period [13]. The determination of the effect of coke on reactions by analysing the influence of total coke formation on the product distribution is not straightforward. Coke formation rate is expected to increase with increasing temperature according to the Arrhenius equation. Higher temperature, on the other hand, increases the desorption rate of coke components [3]. To further look into the effect of coke on the reaction, it is better to distinguish coke into coke precursors and hard coke [3]. The retention of coke precursors is mainly due to trapping and/or condensation in the zeolite pores which is strongly affected by the temperature. While the retention of hard coke is primarily caused by the strong adsorption on the acid sites and low volatility of the formed coke molecules which is negligible even at high temperatures [14]. The understanding in depth of formation of coke and product distribution allows the further development of improved catalysts being less sensitive to deactivation and improvement of desired products yield.

The scope of the present work was to study the product distribution and catalyst deactivation during 1-pentene reaction over HUSY zeolite at different reaction conditions. Alkenes are more reactive towards coke formation than alkanes with same carbon number [3,14] making an olefin feed advantageous for our deactivation studies. 1-Pentene was chosen as model compound that allowed to work with a relatively simple reaction scheme and focus on deactivation studies without any ambiguities caused by the complexity of the reaction system. The effects of time-on-stream (TOS) and reaction temperature on product distribution and catalyst deactivation were investigated.

2. Experimental

2.1. Materials

The HUSY 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

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doi:10.1016/j.cej.2008.02.018

532.4 m^2/g and the micropore volume was 0.26 cm^3/g. BET surface area was 590 m^2/g. The catalyst was pressed into pellets, crushed and sieved, producing particles in the size range of 1.0–1.7 mm. Before each reaction, the catalyst was calcined in an oven at 873 K for 12 h. 1–-Pentene (99% purity, with the impurities not expected to affect the results) was supplied by Sigma–Aldrich Chemicals. Nitrogen (CP grade) was supplied by BOC and used as carrier gas.

2.2. Experimental setup

Catalytic reactions of 1-pentene over HUSY zeolite were carried out in the temperature range of 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). Steel wool was used in the reactor above and below the catalyst bed to ensure isothermal conditions. The catalyst bed was placed between two metal meshes to ensure isothermicity, and it was indeed checked to be isothermal using a movable thermocouple inserted in a small vertical metal protection tube that was placed in the centre of the reactor circular cross section. When placing the thermocouple at different positions along the catalyst bed, the measured temperature readings were the same. Two streams of carrier gas were used in order to avoid condensation at possible cold spots in the rig. One route passed through a saturator placed in a heated water bath at 298 K containing 1-pentene and then mixed with another route of pure carrier gas. By adjusting the flow rates of the two streams, the reactant can reach the desired composition in the nitrogen-reactant feed. In these experiments, the reactant partial pressure was $P_{\text{1-pentene}} = 0.8$ bar ($P_{N_2} = 0.2$ bar), the weight hourly space velocity was WHSV = 86.211 h^{-1}, and the residence time at different reaction temperatures was as followed: $\tau_{523\,K} = 0.062$ s, $\tau_{573\,K} = 0.057$ s and $\tau_{623\,K} = 0.052$ s.

As the experiments were carried out at short time-on-stream, it was vital to ensure that the feed composition was the same throughout the experimental run. Therefore, the reactant feed was directed to the fume cupboard for 15 min until steady state of the feed stream was established while the catalyst bed was purged by carrier gas. Then the constant composition feed stream of 1-pentene and nitrogen was switched to the reactor using a four-way valve. This was the time zero of the experimental run. Products were collected in a heated 10-way sampling valve at specified TOS, namely 1, 2, 3, 5, 7, 9, 12, 15 and 20 min. Upon completion of the experiment, the samples were analysed by a Hewlett Packard 5890 packed series: 2 gas chromatograph equipped with a flame ionization detector (FID), using a 100 m nonpolar DB-Petro (J&W Scientific) capillary column (100 m × 0.25 mm × 0.5 μm). At the end of the experimental run, the saturator was bypassed and the reactor cooled down for 10 min under nitrogen atmosphere. Then the reactor was disconnected from the rig and put in ice for quick cooling to ambient temperature. Coked samples were obtained at 1, 2, 3, 7 and 20 min of TOS and analysed by a method described in previous work [3] using a thermal gravimetric analysis (TGA) apparatus, Cahn TG 131.

The GC peak area fractions were accepted as the mass fractions of the corresponding reaction components [15]. By dividing with the molar mass and renormalising the results, the mass fractions were converted into the corresponding mole fractions as explained in previous work [16]. This method assumes that the outlet hydrocarbon mass flow is equal to the inlet reactant mass flow. This is not strictly valid because some of the hydrocarbons are converted into coke, which cannot be accounted for, as it is not a gaseous product and consequently not analysed by GC. Experimental results from the very first minute of the reaction however, indicated that by far the majority of coke was formed during this period. Hence, the conversion calculated by the above method might not be accurate for the first minute. Even for the first minute though, the calculated conversion value represents the fraction of the reactant not converted to coke that reacted to gaseous products. Anyhow, this conversion calculation was valid after the second minute of reaction, from which the coke formation rate was drastically decreased. We illustrate the above with the following example. At the experimental run with 80% 1-pentene at 523 K, 50 mL/min N_2, the mass inlet flow of 1-pentene was 0.5726 g/min, while the coke formed in the first minute was 0.167 $g_{\text{coke}}/g_{\text{cat}}$ or 0.1086 g of coke, i.e., its average formation rate was 0.1086 g/min. Hence, in the first minute, 18.97% of hydrocarbon feed was converted to coke. The coke formation rate drops during the next 2 min to less than 0.0162 g/min, which is less than 2.8% of the 1-pentene mass feed rate. In future work, the use of an internal standard added to the reactor effluent should overcome this problem.

In order to take account of the fast deactivation at the first minute on stream two conversions have been used, one based on the reactant 1-pentene, $X_{\text{1-C}}$, and a second one based on all linear pentene isomers (1-pentene, *cis*-2-pentene and *trans*-2-pentene), $X_{\text{all-linear-C}}$:

$$X_{1-C_5=} = \frac{\overset{o}{N}_{1-C_5=,\text{in}} - \overset{o}{N}_{1-C_5=,\text{out}}}{\overset{o}{N}_{1-C_5=,\text{in}}}$$

$$X_{\text{all-linear}-C_5=} = \frac{\overset{o}{N}_{1-C_5=,\text{in}} - \overset{o}{N}_{\text{all-linear}-C_5=,\text{out}}}{\overset{o}{N}_{1-C_5=,\text{in}}}$$

where

$\overset{o}{N}_{1-C_5=,\text{in}}$ is the molar flow of 1-pentene at inlet of the reactor,
$\overset{o}{N}_{1-C_5=,\text{out}}$ is the molar flow of 1-pentene at exit of the reactor,
$\overset{o}{N}_{\text{all-linear}-C_5=,\text{out}}$ is the molar flow of all-linear-pentene isomers at exit of the reactor,
$X_{\text{1-C}}$ describes all reactions including double bond isomerisation, while $X_{\text{all-linear-C}}$ includes only cracking/oligomerisation/hydride transfer reactions.

2.3. Coke content estimation

As described in previous work [3], around 150 mg coked sample was heated first 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. Secondly, the temperature was raised to 873 K at a rate of 10 K/min and kept for 30 min under nitrogen flow (60 mL_N/min). During this period coke precursors were removed resulting into a sample weight decrease. By switch from nitrogen to air at the final temperature (873 K) and at the same flow rate, the hard coke deposited on the catalyst was burnt off and 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 switching from nitrogen to air, when the hard coke was completely burnt off. Total coke amount is the sum of coke precursors and hard coke. All coke concentration, expressed in percentage, were estimated by dividing the corresponding coke amounts by the mass of catalyst, which corresponds to the sample mass at the end of TGA procedure after the burning of coke.

3. Results and discussion

3.1. Product distribution

Experiments in the absence of catalyst at different reaction temperatures (523–623 K) did not produce any detectable amounts of any products. The product distribution of 1-pentene reactions over HUSY zeolite at various reaction temperatures is presented in Figs. 1–3. The major products observed were:

- Double bond isomers (DbI): *trans*-2-pentene (*t*-2-C_5=) and *cis*-2-pentene (*c*-2-C_5=);
- Skeletal isomers (SkI): 2-methyl-1-butene (2-m-1-C_4=) and 2-methyl-2-butene (2-m-2-C_4=);
- Cracking (Cr) products: isobutene (*i*-C_4=) and propene (C_3=);
- Hydride transfer (HT) products: *n*-pentane (*n*-C_5) and 2-methylbutane (2-m-C_4).

GC analysis detected other hydrocarbons in amounts much less than 1%. Based on the product distribution, a reaction network was suggested as shown in Fig. 4 [17] modified according to specific findings of this work. Since ethene is very easy to form coke [10], octene [16] and hexene [3] are easy to further crack, they were not detected more than 1% even at initial stage of the reaction.

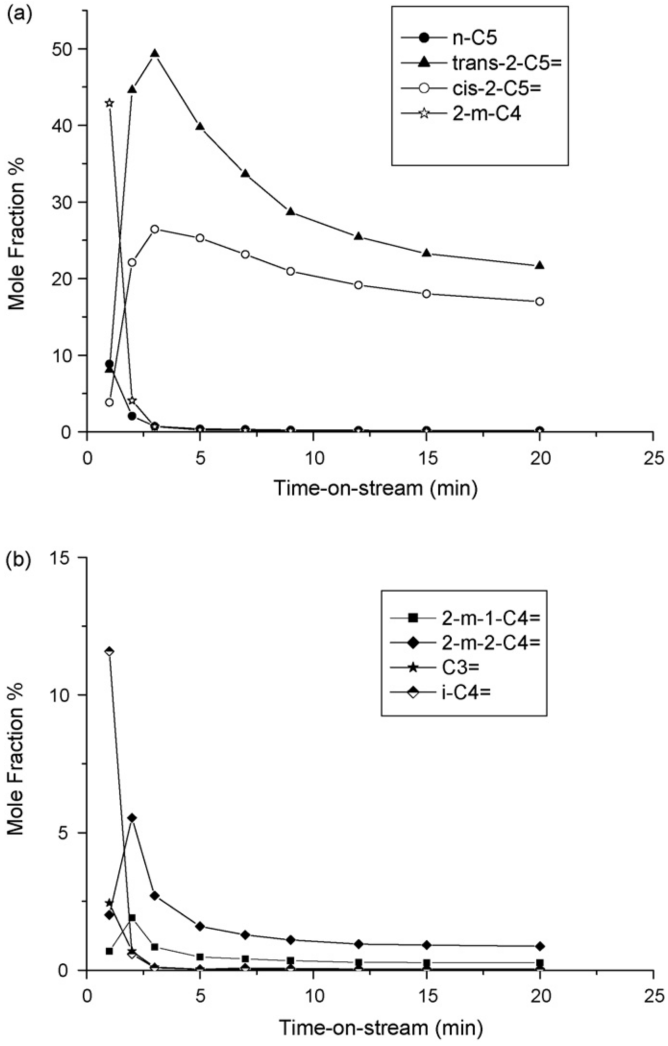

Fig. 1. (a) Distribution of products in large amounts during 1-pentene reactions over HUSY zeolite at 523 K. (b) Distribution of products in small amounts during 1-pentene reactions over HUSY zeolite at 523 K (see text for product symbols in Section 3.1).

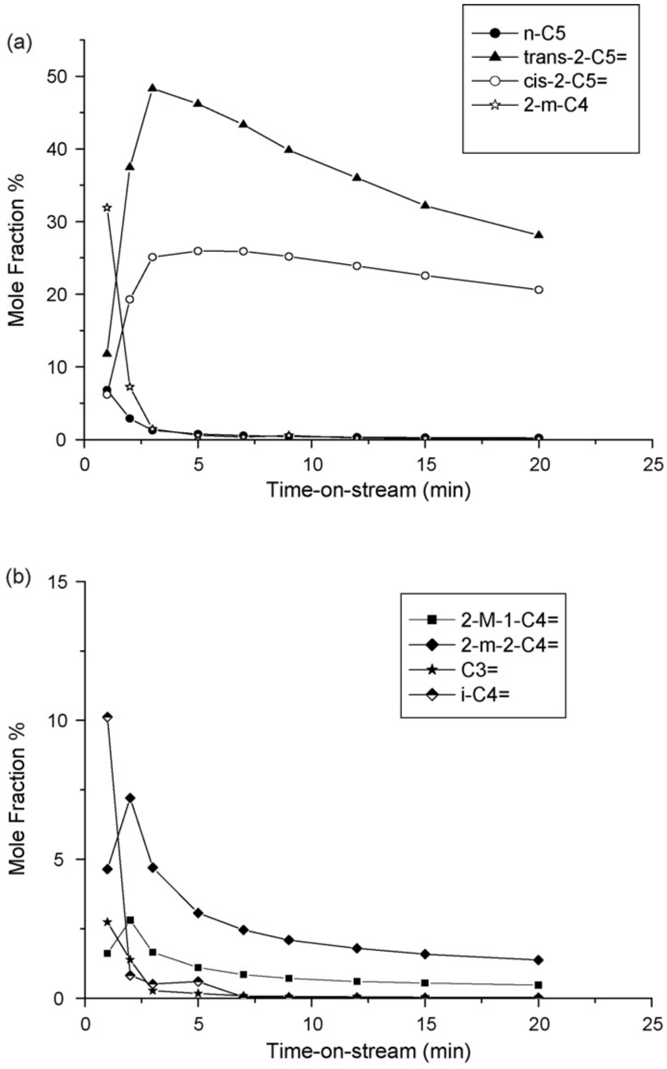

Fig. 2. (a) Distribution of products in large amounts during 1-pentene reactions over HUSY zeolite at 573 K. (b) Distribution of products in small amounts during 1-pentene reactions over HUSY zeolite at 573 K (see text for product symbols in Section 3.1).

Initially, hydride transfer and cracking were the predominant reactions rather than isomerisation. At 1 min TOS and 523 K, the products by hydride transfer- and cracking-reactions accounted for 51.7% (2-m-C_4: 42.9%, *n*-C_5: 8.8%) and 14.1% (*i*-C_4=:11.6%, C_3=:2.5%), respectively. Correspondingly, at 573 K, hydride transfer and cracking products accounted for 38.7% (2-m-C_4: 31.9%, *n*-C_5: 6.8%) and 12.8% (*i*-C_4=:10.1%, C_3=:2.7%), while 59.5% (2-m-C_4: 50.1%, *n*-C_5: 9.4%) and 17.1% (*i*-C_4=:12.6%, C_3=:4.5%) at 673 K. However, these products decreased drastically during the initial stage, indicating a fast deactivation of these hydride transfer- and cracking-reactions. These observations concerning the decrease of hydride transfer can be ascribed to a very rapid formation of coke at the initial stage of the reaction. Since coke components are hydrogen poor with a carbon-to-hydrogen ratio (C/H) much larger than this of the reactant [1,2], hydrogen is transferred during coking from coke precursors to olefinic surface species which desorb as paraffinic products. Formation of paraffins – *n*-pentane, 2-methylbutane (isopentane) and isobutane– in these reactions, is enhanced by hydride transfer at initial TOS. As the intermediate hydrogen

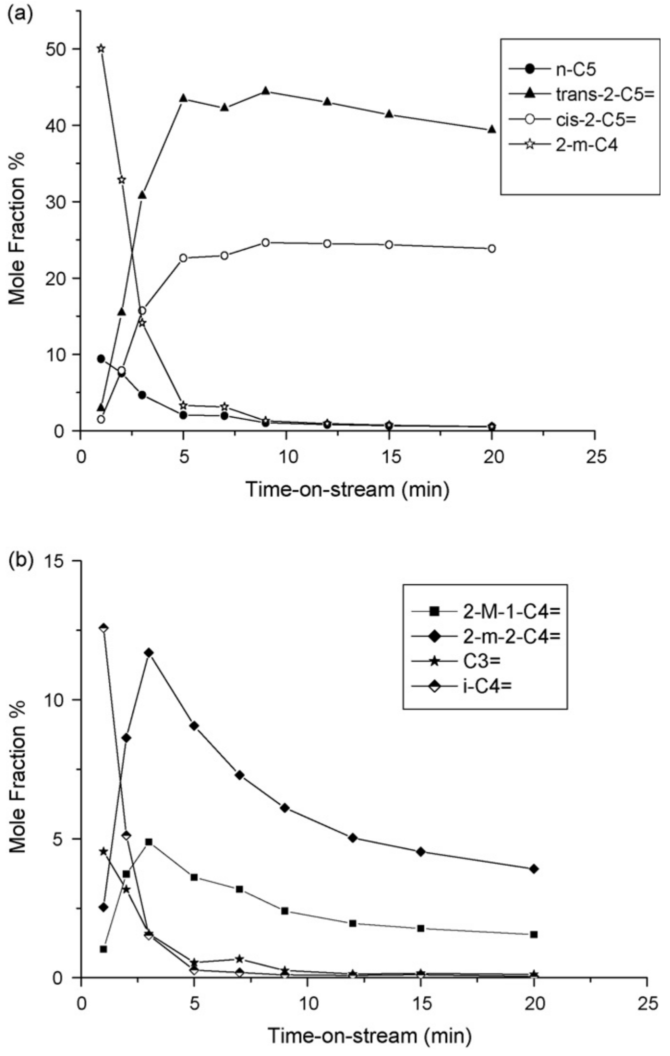

Fig. 3. (a) Distribution of products in large amounts during 1-pentene reactions over HUSY zeolite at 623 K. (b) Distribution of products in small amounts during 1-pentene reactions over HUSY zeolite at 623 K (see text for product symbols in Section 3.1).

decreased in conjunction with a sharp decrease of coking rate, no more hydrogen was available for hydride transfer to form paraffins resulting in a sharp drop of the yield of *n*-pentane, 2-methylbutane and isobutane from 1-pentene. Lower surface concentrations of carbenium ions associated with acid site coverage lead to lower hydride transfer rates. Besides site coverage however, strong pore blockage might occur that would hinder the formation of the bulky hydride transfer reaction transition state.

As explained above, hydride transfer and cracking products experienced a steep decline at 1 min of TOS, while isomer mole fractions increased followed by a slow deactivation. This initial increase of double bond isomers, *trans*- and *cis*-2-pentene, is indicative of the behaviour of intermediate products. It suggests that at the initial stage *trans*- and *cis*-2-pentene oligomerise and react further to cracking products at a much higher rate than the rate they are formed from the reactant 1-pentene. After 3 min of TOS, the only remaining products in significant amounts were 1-pentene isomers, i.e. *trans*-2-pentene, *cis*-2-pentene and small amounts of branched isomers, 2-methyl-2-butene and 2-methyl-1-butene, indicating a steep decrease of the oligomerisation–cracking activity. We would like to emphasise that the blank experiments in the absence of catalyst did not produce any pentene isomers. The only reactions taking place after 3 min at the three different temperatures were isomerisations and mainly double bond isomerisations rather than skeletal ones. Furthermore, the thermodynamically favoured *trans*-2-pentene was formed in larger amounts than *cis*-2-pentene at all conditions. *Cis*-2-pentene mole fraction however, was nearer to the equilibrium value and showed a much slower decline than *trans*-2-pentene. Chemical reaction equilibrium calculations with Gibbs energy of formation data taken from [18] result into the following compositions:

At 523 K; 1-pentene: 3.6%, *cis*-2-pentene: 19.4%, *trans*-2-pentene: 77.0%.
At 573 K; 1-pentene: 3.9%, *cis*-2-pentene: 18.2%, *trans*-2-pentene: 77.9%.
At 623 K; 1-pentene: 4.1%, *cis*-2-pentene: 17.3%, *trans*-2-pentene: 78.6%.

Although strong coking took place in the first minute that resulted into all strong acid sites being occupied by coke [19], the

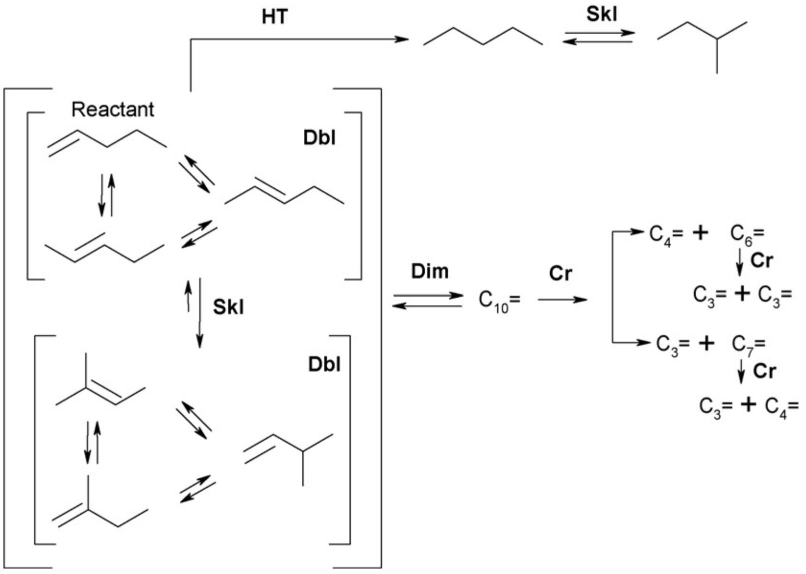

Fig. 4. Reaction network of 1-pentene reaction based on reaction scheme suggested in [17].

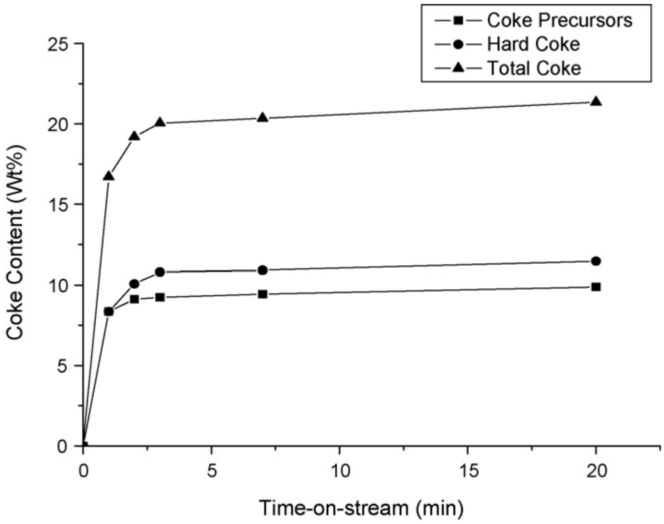

Fig. 5. Coke content during 1-pentene reactions over HUSY zeolite at 523 K.

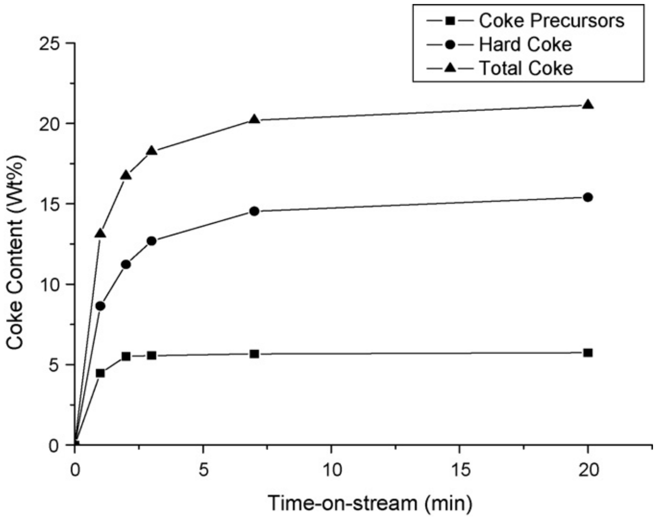

Fig. 7. Coke content during 1-pentene reactions over HUSY zeolite at 623 K.

rest of the acid sites were enough to catalyse double bond isomerisation at high extent. Over strong acid sites the selectivity towards hydride transfer/cracking reactions compared to isomerisation was very high. Hence, almost all 1-pentene which come into contact with strong acid sites convert into corresponding products with almost no isomers formed, as they undergo further cracking reactions. However, the selectivity picture over weak acid sites reverses converting 1-pentene exclusively to isomers. Hence, isomerisation yields showed a drastic increase. The product distribution profiles with TOS (Figs. 1–3) show a remarkable synchronisation between the decline of hydride transfer/cracking and the raise of isomerisation reactions. Comparing cracking and hydride transfer products at three different reaction temperatures, it can be observed that the initial time interval where the rapid decline takes place decreases as the reaction temperature decreases. Considering the coking in the first three minutes of TOS (Figs. 5–7), the amount of total coke increased slowly at high temperatures than that at lower temperatures. This was mainly due to slow hard coke increase.

In order to study the product distribution in more details, 1-pentene reaction over HUSY zeolite at 623 K was carried out only for much shorter time-on-stream, 3 min, allowing more often sampling. Products were sampled at every 20 s in the first 180 s TOS. The product distribution is presented in Fig. 8. It can be clearly seen that the hydride transfer products decreased rapidly, 2-methylbutane decreased from 46.3% at 20 s TOS to 1.6% at 180 s TOS and *n*-pentane decreased from 7.5% at 20 s TOS to 1.7% at 180 s TOS. This observation confirms the above explanation of limitation of hydrogen from transformation of hydrogen-rich reaction components to hydrogen poor coke components. The cracking products also decreased, isobutane decreased from 22.7% at 20 s TOS to 0.2% at 180 s TOS and propene decreased from 7.5% at 20 s TOS to 1.7% at 180 s TOS, respectively. The decrease for cracking products can be explained by the fast catalyst deactivation. The fast coke formation induced poisoning of the acid sites, especially the strong ones. In addition, the deposited coke would decrease the diffusion rate of alkenes to part with the acidic sites and would reduce the free space around the acid sites available for the formation of the bulky intermediates of bimolecular reactions [7]. However, during the initial TOS during which hydride transfer and cracking experienced a steep decrease, double bond isomerisation products, *trans*-2-pentene and *cis*-2-pentene increased. On the other hand, higher reaction temperature favoured formation of more double bond isomerisation products

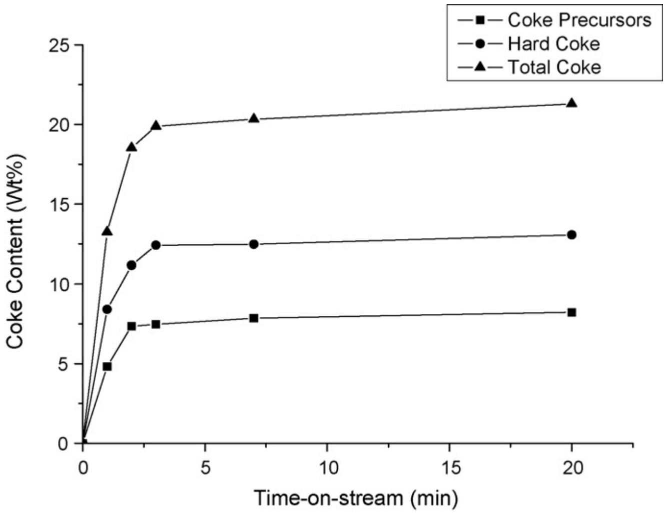

Fig. 6. Coke content during 1-pentene reactions over HUSY zeolite at 573 K.

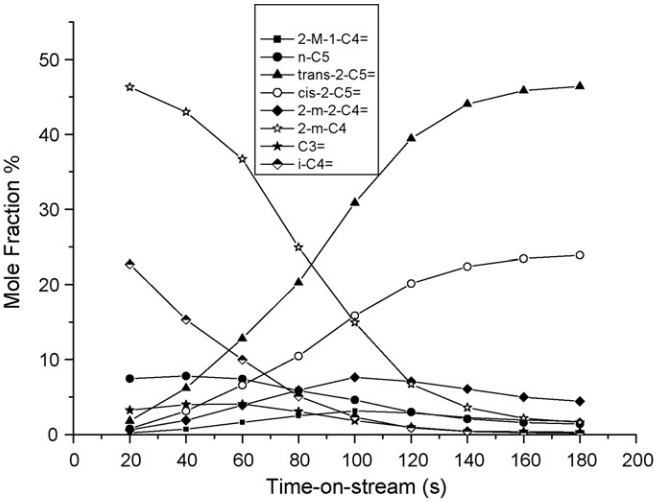

Fig. 8. Product distribution of 1-pentene reaction over HUSY zeolite at 573 K in short TOS.

whose decline was much slower for the same reason that the overall conversion shows an apparent slower decrease at higher temperatures (see Section 3.2). All acidic solids, regardless of their cracking ability, isomerise alkenes [2]. Cracking and skeletal isomerisation as reactions with higher activation energy need stronger acid sites which are deactivated faster [19].

3.2. Conversion

The conversion of 1-pentene versus TOS is shown in Fig. 9a for three different reaction temperatures. As expected the conversion levels were higher at higher temperatures although initially the conversion was almost 100% at all reaction temperatures. The conversion eventually decreased at all temperatures showing an apparent slower deactivation at higher temperatures. Surprisingly, the conversion decrease did not match the steep increase of coke amount at the initial reaction stage (TOS: 0–3 min).

As discussed above, during the first minute of TOS the conversion was exclusively due to hydride transfer/cracking reactions, while later it was due to isomerisation reactions. In order to take into account the different deactivation behaviour of various reaction groups, the conversion of all pentene linear isomers (1-pentene, *cis*-2-pentene and *trans*-2-pentene) was also calculated as explained in Section 2.2. This conversion excludes double bond isomerisation. It accounts for all other reactions that undergo rapid deactivation as reflected in the plot of the conversion of all pentene linear isomers (Fig. 9b). This rapid deactivation phase was also steeper at lower reaction temperatures. Furthermore, Fig. 9b shows that the initial conversion (TOS = 1 min) of all pentene linear isomers is clearly below 100% and distinctively different at various reaction temperatures; just above 90% at 623 K, below 85% at 573 K and just above 70% at 523 K. The reason for the conversion of 1-pentene being almost 100% at the same TOS is that whatever 1-pentene has not undergone hydride transfer- or cracking-reactions isomerises relatively readily to *cis*- or *trans*-2-pentene. This suggests that at 1 min there were enough free weak slow deactivating acid sites for the isomerisation to take place [19]. The higher conversions are simply due to the Arrhenius relationship. Similar amounts of acid sites result into higher reactivity at higher temperatures leading to an apparent slower deactivation at higher temperatures (Fig. 9a and b).

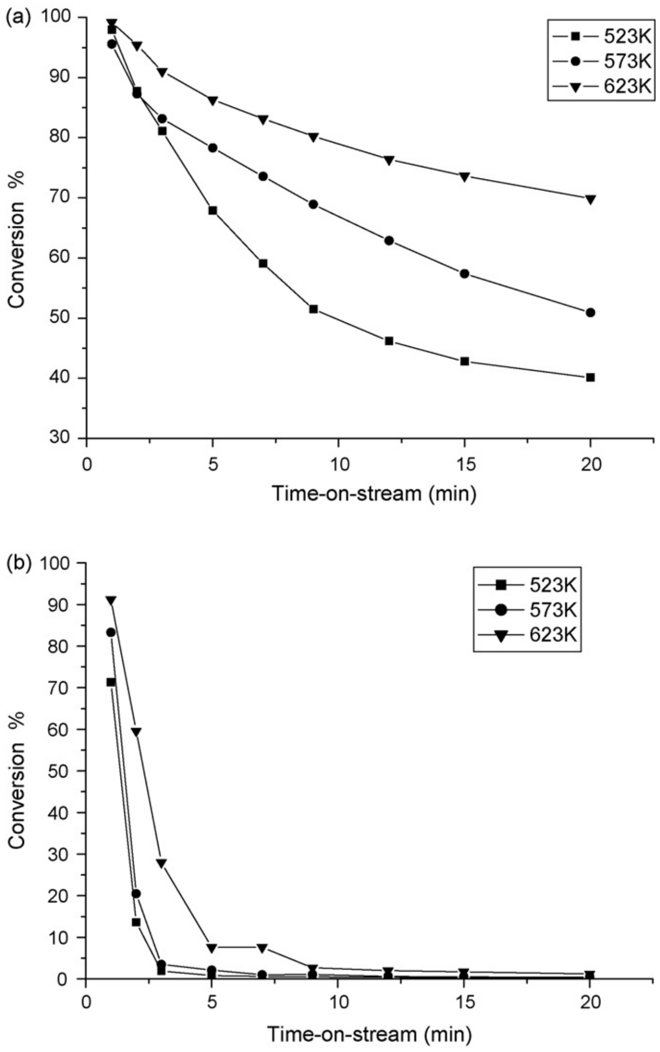

Fig. 9. (a) Conversion of 1-pentene over HUSY zeolite at various reaction temperatures. (b) Conversion of all linear pentene isomers over HUSY zeolite at various reaction temperatures.

3.3. Coke formation

Since the initial coke is most important for the catalyst deactivation study [20], the effect of reaction time (i.e. TOS) in the first 20 min on the coking behaviour of 1-pentene reaction over HUSY zeolite at different reaction temperatures was investigated. As we can see from Figs. 5–7, presenting the total coke content of 1-pentene reaction over HUSY zeolite at 523, 573 and 623 K, the coke content at all these three reaction temperatures was quite high, about 21% at 20 min of TOS. Furthermore, it is fairly obvious that coke formation is an extremely rapid process at the beginning of catalyst exposure to the reaction mixture. The formation rate of total coke is very high during the first minute, whereas it becomes much lower afterwards, similarly to 1-octene reaction [21]. After 3 min, the total coke content shows a linear dependence on TOS which is also in good agreement with previous work [21]. In the first minute, 16.7%, 13.2% and 13.1% ($g_{coke}/g_{cat} \times 100$) content of total coke were produced at 523, 573 and 623 K, respectively. Although the total coke amounts at the first minute were quite high, the initial conversion was extremely high at all three reaction temperatures suggesting that the available catalytic acidic sites are sufficient for cracking. Hence, the cracking ability seemed unaffected by reaction temperature during initial TOS. However, the temperature has an effect on the condensation of coke components resulting to coke precursors volatilising and/or desorbing more easily at higher temperatures. Although, the amount of coke at the end of the reaction (20 min) was almost the same, the initial coking rate at high temperatures was a little lower than that at low temperatures because of the lower condensation of coke components at high temperatures. For example, at 2 min TOS, coke content was 19.2%, 18.5% and 16.7% for 523, 573 and 623 K. Less coke at high reaction temperature results in high conversion. Since coke is formed preferentially on the strongest acid sites and causes their deactivation, the initial deactivation effect of coke is more pronounced than it would be if all of the acid sites were of the same strength [21–23].

Classification of coke into coke precursors and hard coke was carried out [3]. As shown in Figs. 5–7, both coke precursors and hard coke increased with increasing TOS. Both showed a fast coke formation in the first minute TOS and linear time dependence after the first minute especially for hard coke. It can be assumed that hard coke has an unsaturated character. By comparing the colour of coke precursors and hard coke, we found coke precursors were brown while hard coke was black indicating that the latter is more aromatic than coke precursors. Regarding coke colour studies, we observed the following: the originally brown coked catalyst was

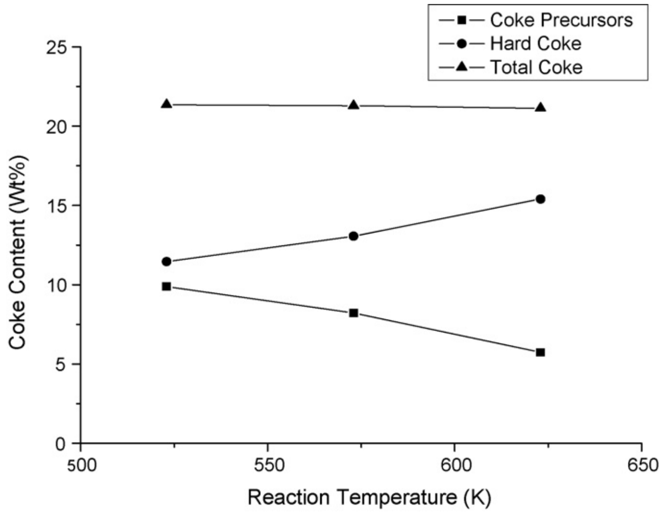

Fig. 10. Coke content after 20 min time-on-stream during 1-pentene reactions over HUSY zeolite at different reaction temperatures.

heated to 873 K with 10 K/min in nitrogen flow and then cooled down to room temperature, i.e. it underwent the treatment where coke precursors had been removed leaving only hard coke. The colour of the final catalyst state, i.e. hard coke, was black. This can be explained as following: coke precursors continuously grow larger causing the size of the surface oligomers to continue to grow and eventually form polyaromatic hard coke [4]. Hard coke being very aromatic in character has a black colour, while coke precursors containing much less polyaromatics have a much lighter colour. The ratio of coke precursors to hard coke in a coked catalyst sample determines the overall sample colour. This is confirmed by comparing the colour of the coked catalyst samples at different reaction temperatures and the corresponding ratios (Figs. 5–7); brown at 523 K (ratio of hard coke to coke precursors = 1.0–1.2), dark grey at 573 K (ratio of hard coke to coke precursors = 1.5–1.7) and black colour at 623 K, respectively (ratio of hard coke to coke precursors = 1.9–2.7).

From Figs. 5–7, it can be also observed that hard coke content is higher than coke precursors during the whole reaction process at all three different reaction temperatures. At 523 and 573 K, after 1 min TOS, both coke precursors and hard coke were formed by the very similar rate while the formation rate of hard coke is slightly higher than coke precursors at 623 K. Moreover, the difference in coke content between coke precursors and hard coke increases with increasing reaction temperature although the amount of total coke is similar. It shows that the individual amount of coke precursors and hard coke is more influenced by reaction temperature rather than the amount of total coke. The effect of reaction temperature on the amount of coke precursors, hard coke as well as total coke is shown in Fig. 10. These results indicate that the total amount of coke nearly stays the same with reaction temperature, the amount of coke precursors decreases with increasing reaction temperature while the amount of hard coke increases. This behaviour can be explained by the high volatility of coke precursors with increasing reaction temperature and their removal into gas phase [3]. The hard coke formation, however, increases with temperature as an activated reaction process as predicted by Arrhenious behaviour.

4. Conclusions

- During 1-pentene conversion over HUSY zeolite, cracking and hydride transfer were predominant reactions only in the first couple of minutes experiencing a rapid deactivation, giving rise afterwards to isomerisation reactions, especially double bond isomerisation. The main products after 3 min of TOS were *trans*- and *cis*-2-pentene.
- Coke formation was an extremely rapid process at the beginning of catalyst exposure to the reaction mixture. Coke content was particularly high during the first minute of TOS while its formation became much slower afterwards.
- The initial hydride transfer products were formed due to the release of hydrogen during the transformation of hydrogen-rich gas phase reaction components to hydrogen poor coke components on the catalyst surface.
- At all temperatures higher amount of hard coke was formed than coke precursors during the deactivation. The amount of coke precursors decreased with increasing reaction temperature due to high desorption of coke precursors into gas phase while hard coke amount increased with temperature as expected from an activated process.

Acknowledgements

The financial support of Overseas Research Students Awards Scheme and K.C. Wong Scholarship are gratefully acknowledged.

References

[1] K.A. Cumming, B.W. Wojciechowski, Catal. Rev. -Sci. Eng. 38 (1996) 101.
[2] Y.V. Kissin, Catal. Rev. -Sci. Eng. 43 (2001) 85.
[3] S. Chen, G. Manos, Catal. Lett. 96 (2004) 195.
[4] M. Guisnet, P. Magnoux, Appl. Catal. A: Gen. 212 (2001) 83.
[5] A.V. Ivanov, E. Zausa, N. Essayem, Appl. Catal. A: Gen. 256 (2003) 225.
[6] D. Meloni, D. Martin, M. Guisnet, Appl. Catal. A: Gen. 215 (2001) 67.
[7] X. Zhu, S. Liu, Y. Song, S. Xie, L. Xu, Appl. Catal. A: Gen. 290 (2005) 191.
[8] R. Quintana, J.W. Thybaut, G.B. Marin, Appl. Catal. A: Gen. 314 (2006) 184.
[9] M. Hernandez, A. Gomez, A. Marcilla, Appl. Catal. A: Gen. 317 (2007) 183.
[10] B. Paweewan, P.J. Barrie, Appl. Catal. A: Gen. 167 (1998) 353.
[11] A. Szklo, R. Schaeffer, Energy 32 (2007) 1075.
[12] S.M. Holmes, A. Garforth, B. Maunders, J. Dwyer, Appl. Catal. A: Gen. 151 (1997) 355.
[13] P.D. Hopkins, A.T. Miller, Appl. Catal. A: Gen. 136 (1996) 29.
[14] S. Chen, G. Manos, J. Catal. 226 (2004) 343.
[15] W.A. Dietz, J. Gas Chromatogr. 5 (1967) 68.
[16] A.A. Brillis, G. Manos, Catal. Lett. 91 (2003) 185.
[17] M. Hochtl, A. Jentys, H. Vinek, Appl. Catal. A: Gen. 207 (2001) 397.
[18] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, 4th edition, McGraw-Hill, 1987.
[19] B. Wang G. Manos, The role of strong zeolitic acid sites on hydrocarbon reactions, Ind. Eng. Chem. Res. 47 (2008) 2948.
[20] A. Sirijaruphan, J.G. Goodwin, R.W. Rice, J. Catal. 221 (2004) 228.
[21] A. Brillis, G. Manos, Ind. Eng. Chem. Res. 42 (2003) 2292.
[22] B. Wang, G. Manos, J. Catal. 250 (2007) 121.
[23] B. Wang, G. Manos, Ind. Eng. Chem. Res. 46 (2007) 7977.