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Deactivation studies during catalytic cracking of C_8 aliphatic hydrocarbons over ultrastable Y-zeolite. Conversion and product yield profiles with time onstream

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The deactivation of an ultrastable Y-zeolite during cracking of *n*-octane, isooctane and 1-octene was studied in a fixed-bed reactor. The relative reactivities of the three reactants in increasing order were *n*-octane < isooctane < 1-octene. At high residence times, complete conversion was achieved followed by a relatively slow decline that, in fact, presented a falsified deactivation picture. On the other hand, a surprising olefin yield increase with time onstream was observed, i.e., isobutene during isooctane cracking and octene isomers in the case of 1-octene. The isobutene yield increase was assigned to preferential deactivation of strong acid sites that allowed primary products to desorb into the gas phase, increasing their apparent yield rather than undergo secondary reactions. Similarly, 1-octene isomers showed a yield increase with time onstream due to stronger deactivation of cracking reactions than isomerization.

KEY WORDS: deactivation; catalytic cracking; hydrocarbons; zeolites; acid catalysis.

1. Introduction

The cracking of hydrocarbons on acid solid catalysts is a long-established and a very important industrial process. Their cracking mechanisms run via carbonium or carbenium ion intermediates, similar to reactions catalyzed by strong acids in homogeneous media [1–3]. Carbonium ions play a dominant role in high-temperature paraffin cracking, since they are the initiators of the cracking chain proceeding via complex ionic mechanisms [4,5]. Carbenium ions, on the other hand, are involved in the chain propagation of cracking, skeletal and double-bond isomerization, alkylation and oligomerization reactions [3]. Overall, for the cracking of paraffins, three different pathways have been suggested [6–9].

Albeit tremendous progress has been made in the development of cracking catalysts, they still suffer from strong side reactions that form heavy, low boiling point, high molar mass by-products, the so-called coke, that deposit on the active surface and deactivate the catalysts.

The aim of this work was to study the effect of process variables, like residence time and reactant feed composition, in order to get further insight into the deactivation behavior of the chosen system. The reaction system chosen was the catalytic cracking of aliphatic hydrocarbons over an acidic ultrastable Y-zeolite (USHY). Simple one-component feed streams have been chosen with the same carbon number but with different structure, namely *n*-octane, isooctane (2,2,4 trimethylpentane) and 1-octene. Differences in profiles with time onstream of the product distribution from the three reactants were studied and discussed.

2. Experimental section

2.1. Materials

The USHY zeolite catalyst was provided in calcined powder form of average crystallite size of 1 μm, a bulk 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 in the size range of 1.0–1.7 mm. Before each experiment, the catalyst was dried in an oven at 473 K for 2 h.

All hydrocarbons, *n*-octane, isooctane (2,2,4 trimethylpentane) and 1-octene, were supplied by Fluka Chemicals (99% purity). Nitrogen (99% purity) was used as carrier gas.

2.2. Experimental procedure

The experiments were performed in the temperature range of 523–623 K and at atmospheric pressure, in a stainless steel tubular fixed-bed reactor, with a total length of 25.5 cm and an inner diameter of 15 mm. The 1-cm-long catalyst bed was placed between two metal

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meshes to ensure isothermicity. Experiments in the absence of catalyst were performed with each reactant at the highest temperature (623 K) and lowest flow rate, i.e., highest residence time to test any catalytic activity of these meshes. No components other than the individual reactants were present in the reactor outlet samples that were collected.

The amount of catalyst used in each experiment was 0.5 g. A type-K thermocouple was inserted in a small metal protection tube and placed in the center of the reactor. The carrier gas passed through a saturator placed in a heated water bath at three different flows, namely 25 $\mathrm{mL_N/min}$, 100 $\mathrm{mL_N/min}$ and 190 $\mathrm{mL_N/min}$, whereas the reactant composition was varied between 5, 10 and 20 % by adjusting the temperature of the water bath. Table 1 summarizes the values of residence time at all experimental conditions.

As the experiments were carried out at short times onstream, it was vital to ensure that the feed composition was the same throughout the experimental run. Therefore, the catalyst was purged by a carrier gas for 15 min at every temperature and then the reactor was switched to the stable feed stream of hydrocarbon and nitrogen using a four-way valve. This was the time zero of the experimental run. The experiments lasted for 20 min, and the samples were collected via a multisampling valve at prespecified time periods, namely 1, 2, 3, 5, 7, 9, 12, 15 and 20 min. Upon completion of the experiment, the samples were analyzed by a Perkin Elmer 8410 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). Reproducibility experiments showed an error of ±1%.

2.3. Experimental calculations

A simple method was used to calculate the conversion that was based on the mass fractions of the reactant, which were equal to the chromatographic area fraction [10] of the reactant at the reactor outlet. We show the validity of this, starting with the definition of conversion

$$X_A = (\overset{o}{N}_{Ao} - \overset{o}{N}_A)/\overset{o}{N}_{Ao} = (\overset{o}{m}_{Ao} - \overset{o}{m}_A)/\overset{o}{m}_{Ao}$$
$$= 1 - (\overset{o}{m}_A/\overset{o}{m}_{Ao}) = 1 - (A_A/A_{TOT})$$

where X_A is the conversion of reactant A, $\overset{o}{N}_{Ao}$ is the molar flow of reactant A at the inlet of the reactor, $\overset{o}{N}_A$ is the molar flow of reactant A at the exit of the reactor, $\overset{o}{m}_{Ao}$ is the mass flow rate of reactant A at the inlet of the reactor, which is equal to the total mass flow $\overset{o}{m}_{TOT}$, i.e., the sum of all the hydrocarbon components' mass-flow rates at the outlet, $\overset{o}{m}_A$ is the mass-flow rate of reactant A at the exit of the reactor, A_A is the GC area of reactant A, A_{TOT} is the total GC area of the hydrocarbon reaction components and (A_A/A_{TOT}) is the GC area fraction of A. However, this method assumes that the outlet hydrocarbon mass flow is equal to the inlet reactant mass flow. This is not strictly valid, as some of the hydrocarbons are converted to coke, which could not be accounted for, as it was not a gaseous product and consequently not analyzed by the GC. Experiments performed at the very first minute of the reaction indicated that the highest coking rate was observed during this very first minute [11]. Therefore, since most of the coke was produced at the beginning of each experiment, the conversion calculated by the above method was not 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. However, it must be said that this conversion estimation 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 10% 1-octene at 573 K, 100 $\mathrm{mL_N/min}$ N_2, the mass inlet flow of 1-octene was 0.051 g/min, while the coke formed in the first minute was 0.09 $\mathrm{g_{coke}/g_{cat}}$ [11] or 0.045 g of coke, i.e., its average formation rate was 0.045 g/min. This means, in the first minute, almost 90% of the hydrocarbon feed was converted to coke. The coke-formation rate drops

Table 1
Experimental conditions used in this work

Flow rate (mL/min)	25 (mL/min)	100 (mL/min)	190 (mL/min)	
Temp (K)	Residence time (min)			Reactant feed composition
523	–	0.0044	0.0023	0.05
523	0.0168	0.0042	0.0022	0.1
523	0.0149	0.0037	0.0019	0.2
573	–	0.0040	0.0021	0.05
573	0.0153	0.0038	0.0020	0.1
573	0.0136	0.0034	0.0017	0.2
623	–	0.0037	0.0019	0.05
623	0.0141	0.0035	0.0018	0.1
623	0.0125	0.0031	0.0016	0.2

during the next two minutes to less than 0.002 g/min [11], which is less than 4% of the 1-octene mass feed rate.

3. Results and discussion

3.1. n-*Octane reactions*

The major products of *n*-octane cracking over USHY in the order of significance were isobutane, propane, isopentane and *n*-butane. GC analysis detected other molecules in the range of C_2–C_6 hydrocarbons, with a product yield of less than 2%. The *n*-octane conversion at two reactant feed compositions, 10 and 20%, and various temperatures, is presented in figure 1. The initial rapid increase was indicative of an induction period toward steady state. At the first minutes (0–3 min), the curve shapes might not represent the exact conversion versus time profiles as they belong to this induction period. This is illustrated in figure 2 in the example of isobutane mole fractions in the product stream. As this induction period is not portrayed by the experimental curves, a possible real curve adjusting for the transitional character of an induction period is added next to the experimental values. It is during this induction period that the strongest coking takes place corresponding to the deactivation of the strongest acid sites [11]. The following decline of the conversion values in the case of *n*-butane was relatively mild, indicative of a relatively mild coking compared with the other C_8 reactants [11].

3.2. *Isooctane reactions*

Isooctane was chosen as the representative of the second type of compounds used in catalytic cracking, that of branched paraffins; the other being straight paraffins and olefins. Unlike *n*-octane and 1-octene reactions, isooctane reactions showed a low selectivity toward *n*-butane (max. of 1% mole fraction). Instead, isobutene was produced in small quantities, nevertheless larger than with the other two reactants. In addition to that, isobutane, isopentane and propane were the other significant products. Other products included ethane, *cis*- and *trans*-butenes and *n*-hexane. However, their maximum yields were less than 1%, and they were not considered as major products.

The effect of residence time can be seen in figure 3, and it is clear that it could present a misleading picture about the catalyst deactivation. As the residence time increased, larger isooctane conversion was obviously obtained. The residence time of the catalytic system at 25 mL_N/min and 623 K was almost four times larger than the residence time at 100 mL_N/min and 623 K. In both cases, the initial conversion, with the very reactive isooctane, reached the maximum value of 100% because of the very high and strong acidity. The number of active sites for the cracking reaction was very high, in order that in both cases, despite a residence time difference at a factor of about 4, the maximum conversion could be achieved. The rapid catalyst deactivation changed the picture later on. A large number of active sites were deactivated in the first couple of minutes. The residence time at 25 mL_N/min was enough to keep the level of conversion at high values, even with the remaining number of active sites, while an almost four times shorter residence time at 100 mL_N/min could not achieve high conversions, resulting in a fast decline of the conversion curves. Consequently, it is clear that high residence time runs could present a falsified picture of deactivation/coking. While high levels of coke were formed in both cases [11], the decline of the conversion curve was much less steep in the case of 25 mL_N/min than in the case of

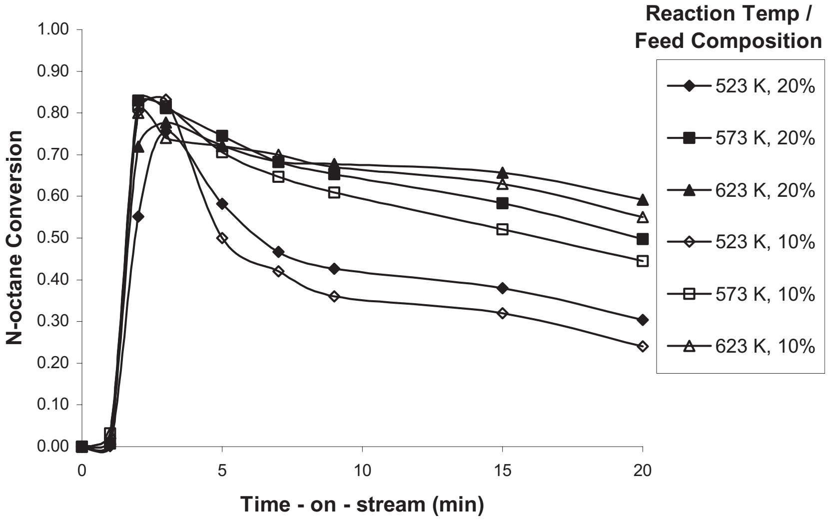

Figure 1. *n*-Octane conversion during cracking over USHY, at different temperatures and reactant compositions.

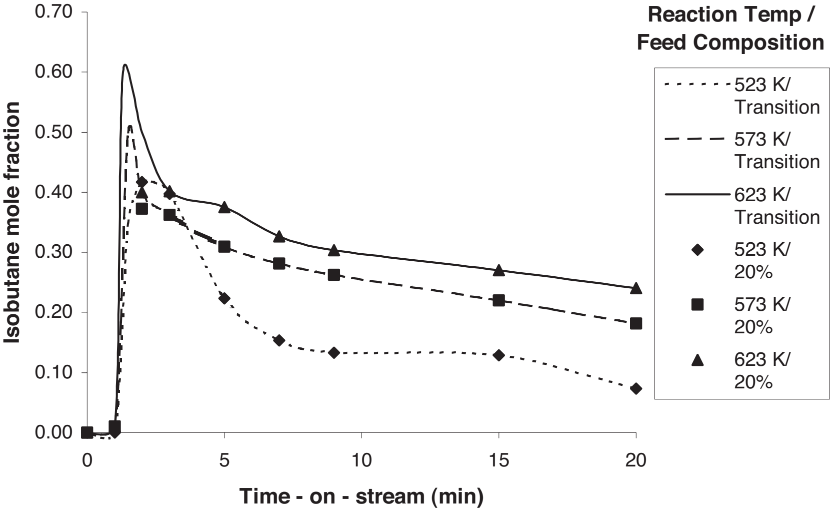

Figure 2. Isobutane mole fraction during *n*-octane cracking over USHY at various temperatures and 20% reactant composition.

100 mL_N/min. The 190-mL_N/min curve showed a much lower initial conversion than 100 mL_N/min and fast deactivation similar to the one at 100 mL_N/min.

Isobutene (figure 4) was produced in not high, yet considerable, amounts. What was of greater importance, however, was the fact that the isobutene yield increased with time onstream (TOS), although catalyst deactivation was in progress. The explanation behind this selectivity shift could lie on preferential deactivation of strong acid sites. Strong acid sites are responsible for strong adsorption of alkenes and catalyzing their further reaction to secondary products. When strong acid sites are not active any more, secondary reactions converting primary olefin products take place at lower degree. More alkenes are desorbed into the gas phase, increasing their apparent yield. This was observed in all reaction runs. The yields of isobutene increased with time, whereas at the same time, the yields of isobutane and other main paraffinic products decreased. Similar increases in isobutene yields with TOS were reported in the literature [12,13], where the explanation given was that isobutene yields increased after carbonaceous deposits were formed on the active sites of the catalyst, deactivating them. Alternatively expressed, the actual residence time decreases with TOS, since less catalytic active sites are available, leading to a selectivity shift.

Similarly, isobutene yields increased with increasing N_2 flow that would increase external mass transfer rates and therefore the net desorption rates. Higher flow enhances net desorption of alkenes from the zeolitic acid sites, reducing their residence time in the zeolite mass and the degree at which they undergo secondary reactions. The increase of the isobutene yield with the volumetric flow further supports the argument of the selective deactivation of strong acidic sites, causing an increase of the isobutene yield with TOS. The intermediate character of isobutene can be clearly seen in figure 5, where its mole fraction shows a maximum with

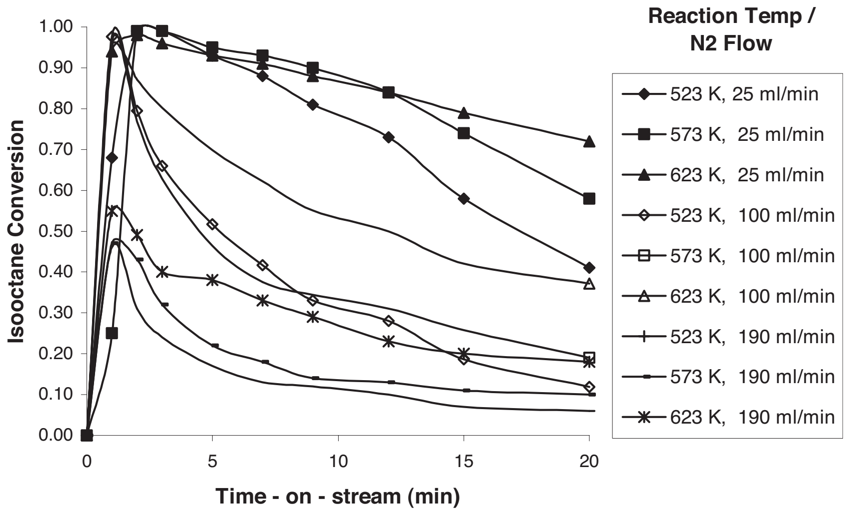

Figure 3. Isooctane conversion during cracking over USHY for different temperatures, at 20% reactant composition and different residence times.

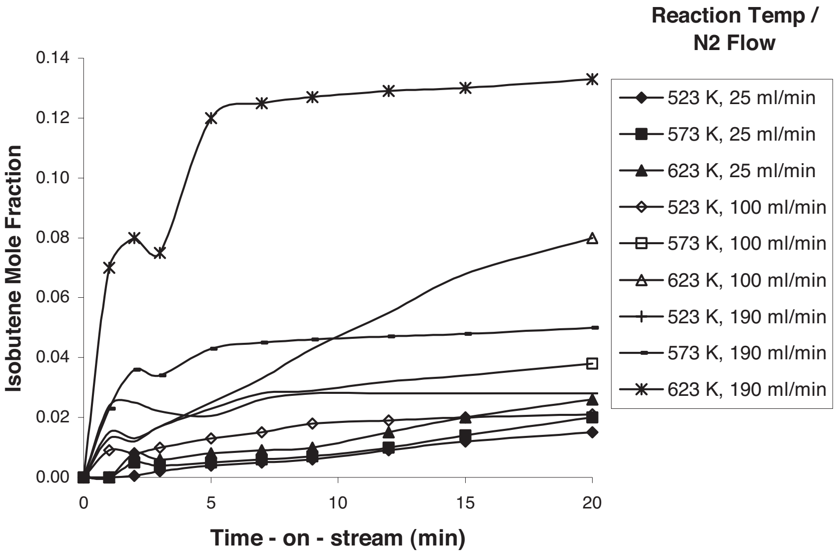

Figure 4. Isobutene mole fraction during isooctane cracking over USHY at various temperatures and residence times.

residence time at various TOS. Higher temperatures leading to higher yields were observed in all experimental runs, as expected.

3.3. 1-Octene reactions

Significant products during 1-octene cracking were isobutane, isopentane, propane, *n*-butane, and 1-octene isomers. There were other products, namely, ethane, propene, 1-butene, isobutene, *cis*- and *trans*-butenes, pentanes and pentenes, hexanes and hexenes, a few C_7 molecules and a few aromatic compounds. However, their yields were lower than 0.02.

From literature [5,14], the cracking of 1-octene takes place via the monomolecular β-scission and/or via the nonclassical carbonium ion, resulting in an olefin and a lighter carbenium ion. Hydrogen transfer reactions between the olefins formed result in the saturation of olefins to paraffins and the formation of aromatics [8,14,15]. In our reaction runs at generally low residence times however, low selectivities for aromatics were observed that were considered to be the final products of a series of consecutive reactions. 1-octene isomers were observed in large quantities whose yields increased with TOS (figure 6). The difference in the isomer yields at various residence times, namely, the much lower values at high residence times ($25\,mL_N$/min N_2 flow), indicated that the 1-octene isomers should be primary products of 1-octene reactions that underwent further cracking reactions, while paraffins were mainly formed by secondary reactions. This conclusion is also supported by the fact that at increased TOS the yield of octene isomers decreased with reaction temperature that enhanced secondary reactions. To clarify the role of each component in the reaction scheme, figures 7 and 8

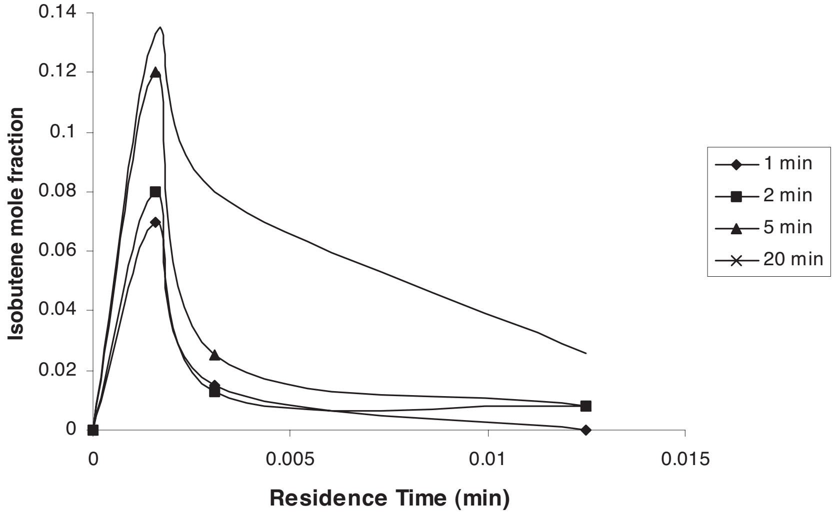

Figure 5. Isobutene mole fraction during isooctane cracking over USHY, at different residence times, different times onstream, 20% reactant composition and 623 K.

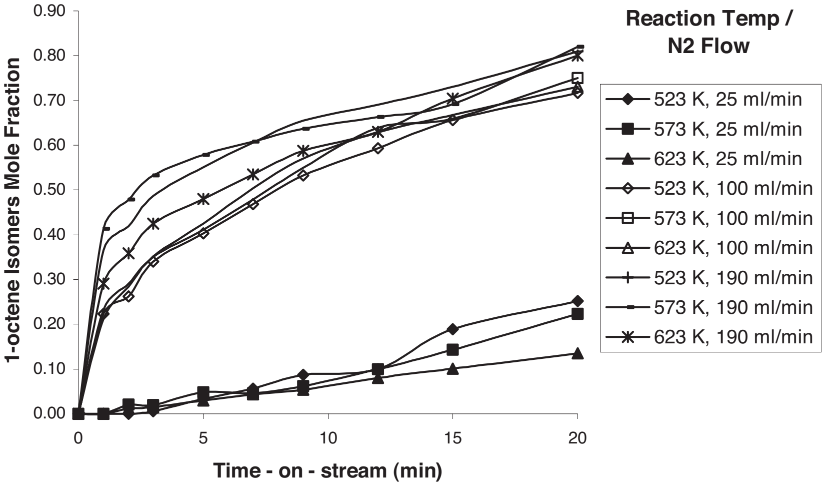

Figure 6. 1-octene isomers mole fraction during 1-octene cracking over USHY, at 10% reactant composition, different temperatures and residence times.

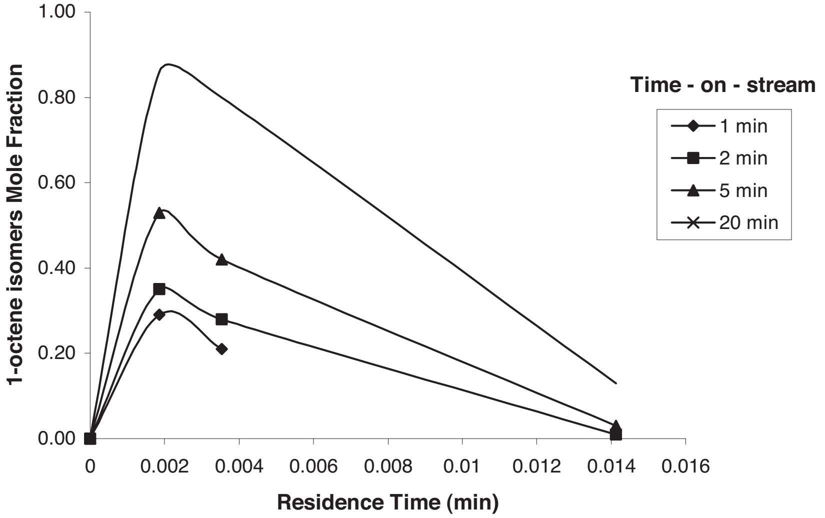

Figure 7. 1-octene isomers mole fraction during 1-octene cracking over USHY, at different residence times, different times onstream, 10% reactant composition and 623 K.

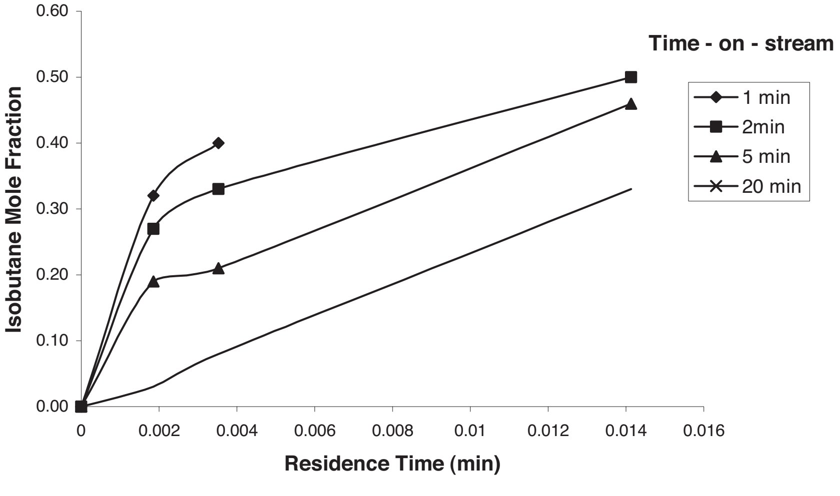

Figure 8. Isobutane mole fraction during 1-octene cracking over USHY, at different residence times, different times onstream, 10% reactant composition and 623 K.

were plotted. The mole fractions of 1-octene isomers and isobutane are plotted against residence time, at different times onstream, for the three sets of experiments with 10% reactant composition and 623 K. From figure 7, the curves of the 1-octene isomers mole fraction show a maximum, confirming that these isomers behaved as intermediates in our reaction scheme, while isobutane (figure 8) was clearly the end product in a consecutive reaction network. Furthermore, the more the catalyst was deactivated, the lower was the extent of cracking of 1-octene isomers compared to 1-octene isomerization, resulting in a higher maximum of their mole fraction. This difference with TOS was quite pronounced at low residence times, but almost nonexisting at the highest value corresponding to N_2 flow of 25 mL_N/min. In this case, the octene isomer molecules had enough time to be further cracked even over a considerably lower number of active sites.

The increase of the octene isomers yield with TOS was faster at low residence times. As already mentioned, 1-octene underwent a rapid isomerization reaction and the octene isomers underwent further cracking. Isomerization took place near its equilibrium and was less affected by catalyst deactivation. For cracking reactions over the deactivated catalyst, the residence time corresponding to 25 mL_N/min was enough to keep the extent of the reactions high, while it was not enough at the 100-mL_N/min experiments, resulting in faster deactivation. Another significant difference was that at low residence times they did not show any differences in their yields with reaction temperature. As for the two reactions, 1-octene isomerization and isomers cracking, the latter was enhanced more by temperature than the first one. Higher temperatures resulted in lower net octene isomer formation. Low residence times decreased the extent of the secondary cracking reactions, minimizing the temperature influence.

What was very different when comparing the cracking of 1-octene with that of *n*-octane or even isooctane was the very high values of 1-octene conversion, due mainly to isomerization. Although a relatively slow decline of 1-octene conversion with TOS was obvious, these conversion values were kept high throughout the 20 min of allowed TOS. Even at the 20th minute, conversion was above 95% at 623 K, while similar conversions were observed for the two lower reaction temperatures.

4. Conclusions

- For all reactants used, isobutane was the product with the highest yield. Yield values of almost 0.9 were observed and maintained at high level throughout the experimental runs during isooctane cracking. Propane, *n*-butane and isopentane were the other major products. However, in isooctane reactions, isobutene was formed in larger amounts than *n*-butane.
- High residence time runs could present a falsified picture of deactivation. The corresponding decline of conversion or yield versus TOS was much less steep than the formation of the corresponding deactivation cause, i.e., coke. At similar levels of remaining active sites, high residence times were able to keep the conversion level considerably higher and present a much slower apparent activity decline.
- During isooctane cracking, isobutene yields increased with TOS because of the preferential deactivation of strong acid sites, resulting in increasing amount of isobutene desorbed into the gas phase with TOS, instead of undergoing secondary reactions.
- Similar picture was observed for octene isomers during the cracking of 1-octene. A stronger deactivation of cracking reactions compared to isomerization resulted in a net increase with TOS of octene isomers. Their formation from 1-octene was deactivated much slower than their consumption in secondary cracking reactions, leading to a net increase of their yield with TOS.
- For the same conditions used, *n*-octane achieved the smallest conversion of all three reactants as expected, since linear paraffin was not very reactive compared to branched paraffins or olefins.
- With 1-octene, a high extent of isomerization reactions, which were less affected by coking, resulted in high conversion levels and high isomer yields. The octene isomers underwent further secondary cracking reactions, contributing strongly to coking.

References

[1] B.W. Wojciechowski, Catal. Rev. Sci. Eng. 40 (1998) 209.
[2] I. Kiricsi, H. Forster, G. Tasi and J.B. Nagy, Chem. Rev. 99 (1999) 2085.
[3] A. Corma, P.J. Miguel and A.V. Orchilles, Appl. Catal. A: Gen. 138 (1996) 57.
[4] F.C. Jentoft and B.C. Gates, Top. Catal. 4 (1997) 1.
[5] Y.V. Kissin, Catal. Rev. Sci. Eng. 43 (2001) 85.
[6] P.G. Smirniotis and E. Ruchenstein, Ind. Eng. Chem. Res. 33 (1994) 800.
[7] S.T. Sie, Ind. Eng. Chem. Res. 31 (1992) 1881.
[8] S.T. Sie, Ind. Eng. Chem. Res. 32 (1993) 397.
[9] S.T. Sie, Ind. Eng. Chem. Res. 32 (1993) 403.
[10] W.A. Dietz, J. Gas Chromatogr. 5 (1967) 68.
[11] A.A Brillis and G. Manos, Ind. Eng. Chem. Res. 42 (2003) 2292.
[12] G.N. Brasco and R.A. Comelli, Catal. Lett. 71 (2001) 111.
[13] Z.R. Finelli, N.S. Figoli and R.A. Comelli, Catal. Lett. 51 (1998) 223.
[14] J.S. Buchanan, J.G. Santiesteban and W.O. Haag, J. Catal. 158 (1996) 279.
[15] A. Corma, M. Faraldos, A. Martinez and A. Misfud, J. Catal. 122 (1990) 230.