Kinetics and Catalysis, Vol. 45, No. 2, 2004, pp. 209–214. From Kinetika i Kataliz, Vol. 45, No. 2, 2004, pp. 225–231.

CATALYTIC REACTION MECHANISMS

n-Octane Dehydrocyclization on $Cr_2O_3/La_2O_3/ZrO_2$ Catalyst Elucidated by H–D-Tracer Experiments[1]

H. Ehwald, M. Bartoszek, and H. Lieske

Institute of Applied Chemistry Berlin-Adlershof, Richard-Willstätter-Str. 12, D-12489 Berlin, Germany

e-mail: ehwald@aca-berlin.de

Received December 12, 2002

Abstract—H–D tracer experiments during *n*-octane aromatization on $Cr_2O_3/La_2O_3/ZrO_2$ catalysts allow conclusions to be drawn on the reaction mechanism. The rate-determining step is the dissociative adsorption of the paraffin molecule. The following dehydrogenation steps seem to proceed predominantly reversibly.

INTRODUCTION

The straight run gasoline reforming and, especially, the C_{6+} paraffin dehydrocyclization (DHC) are important sources of hydrocarbons and of hydrogen, too.

While the hydrocarbon pathway of these reactions has been investigated very intensively [1, 2], less attention has been paid to the hydrogen side of these processes.

Tracing the molecular hydrogen part of the feed mixture using deuterium and the study of *n*-octane dehydrocyclization (DHC), using D-tracer distribution between hydrogen containing components (molecular hydrogen and hydrocarbons) is the easiest method for obtaining information on the dynamics of hydrogen formation and consumption in this complicated reaction network.

Recently [3, 4], we studied the D-tracer distribution within molecular hydrogen during DHC on $Cr_2O_3/La_2O_3/ZrO_2$ catalysts [5]. The results justified assuming an intensive tracer exchange between the hydrogen molecules (homomolecular exchange) and also between molecular hydrogen and hydrocarbons (heteroexchange). Comparing the molecular hydrogen dissociation rates with the DHC rate time behavior, we could confirm that catalyst deactivation is not caused by coke induced mass transport limitations. The number of active sites responsible for the dehydrogenation is directly decreased by coke formation.

The aim of the present work is to study additionally the tracer distribution within the hydrocarbon products to obtain more detailed information about the mechanism of the DHC on $Cr_2O_3/La_2O_3/ZrO_2$. On Pt-containing catalysts, similar work has been done already by Shi and Davis [6].

[1] This article was submitted by the authors in English.

EXPERIMENTAL

Catalyst preparation, conditions of DHC experiments, and the molecular hydrogen tracing methods are described elsewhere [4]. The conditions of the experiments in this paper were as follows: 500 mg catalyst, reaction temperature 550°C, and two different feed rates.

The low feed rate amounted to 125 mmol/h D-tracered molecular hydrogen (tracer concentration 97.5%) and 2.26 mmol/h *n*-octane (*n*-octane saturator at 25°C).

The high feed rate amounted to 375 mmol/h D-tracered molecular hydrogen (tracer concentration 97.5%) and 27.7 mmol/h *n*-octane (*n*-octane saturator at 51°C).

The hydrocarbon product mixture analysis was performed by on-line gas chromatography (HP5890, 30 m capillary column SE30).

The molecular hydrogen isotope analysis was performed by on-line measuring of the ion current intensities at the mass numbers 2 (HH), 3 (HD), and 4 (DD), using a Baltzers QMG 421 mass spectrometer.

To determine the deuterium tracer distribution within the hydrocarbons in the product stream, samples were taken with the help of gas-collecting tubes (200 ml) connected for 45 min to the reactor outlet. The samples were analyzed off-line, using a MD800 GC/MS-System with a 30 m DB5MS column at standard conditions: 70 eV electron impact ionization.

The separation of various deuterated hydrocarbons by gas chromatography becomes possible because of an inverse isotope effect. As shown in Fig. 1 for deuterated C_8-aliphatics, the retention time of hydrocarbons decreases [7] with increasing deuterium content. Perdeuterated and undeuterated C_8-hydrocarbons can be completely separated using weakly polar stationary phases. Small differences of the deuterium content result in incomplete gas-chromatographic separation, but, with the help of a mass spectrometric detector, it becomes possible to determine the individual isotope species of overlapping gas chromatographic peaks.

0023-1584/04/4502-0209 © 2004 MAIK "Nauka / Interperiodica"

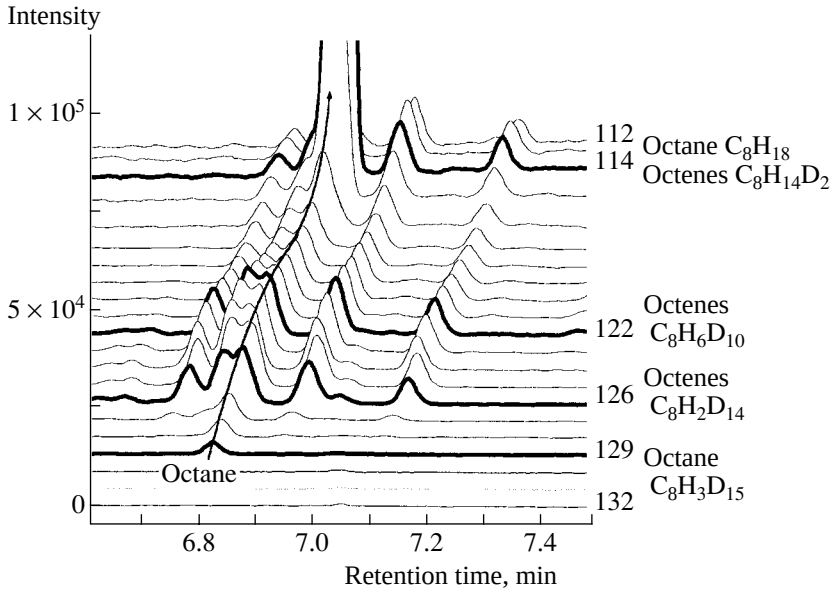

Fig. 1. Mass traces of deuterated *n*-octane and *n*-octene isomers.

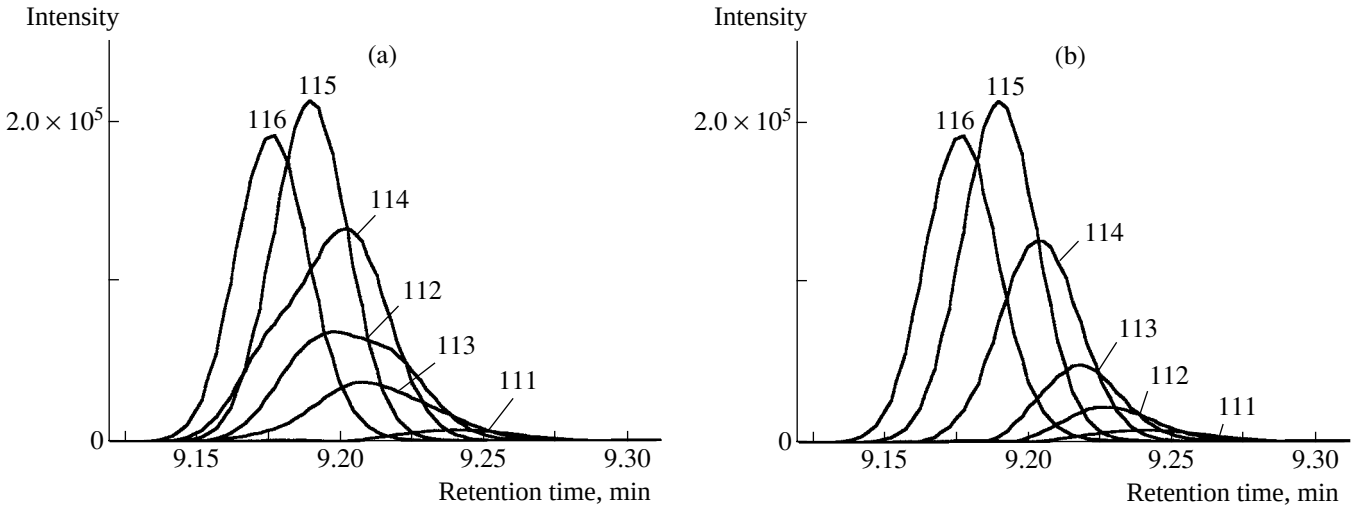

Fig. 2. Ethyl benzene mass chromatograms of (a) raw data and (b) fitted curves.

Some difficulties in the determination of *n*-octane and *n*-octenes arise from the close eluating of *n*-octane and one of the *n*-octene isomers. To get the correct content of both in every trace, we additionally used a peak-fitting program.

The quantitative analysis of aromatic isotopic molecules is much more complicated because of the intensive $[M–H]^+$ (respectively, $[M–D]^+$) fragmentation of aromatics: The molecular ion traces of lower deuterated aromatics are deformed by fragment ion traces of higher deuterated species (Fig. 2a). Subtraction of the fragment ion contribution combined with fitting the peak shape allows the correction (Fig. 2b) of the raw data.

There are no interferences at the maximum mass number ($m/z = 116$) of the C_8-aromatics, and, therefore, this trace is used as a shape model for the peak fitting. The m/z 115 trace is also undisturbed, because the loss of one D-atom by electron impact results in $[M–D]^+$ fragments with m/z 114. Lower traces must be corrected by fitting them. The deuterium distribution of the aromatics was always calculated from the peak areas of the fitted curves [8].

RESULTS AND DISCUSSION

Low feed rate DHC experiments, predominantly used in our former work [3, 4], start with nearly 100%

Table 1. *n*-Octane DHC at 550°C with low feed rate: 250 mmol (g Cat)$^{-1}$ of D-tracered molecular hydrogen and 5.52 mmol (g Cat)$^{-1}$ of *n*-octane

Time	Tracer content of the molecular hydrogen in the product stream			Conversion			
	values measured	calculated without exchange	calculated with products exchange	of *n*-octane	to olefins	to aromatics	to cracking products
min	%	%	%	%	%	%	%
5	83.6	92.7	83.9	98.7	0.4	70.0	28.4
45	84.0	92.8	84.2	96.3	2.2	70.2	23.9
90	85.1	93.0	84.9	90.3	3.5	66.0	20.8
135	86.0	93.4	85.8	83.4	4.1	60.7	18.6
180	87.0	93.7	86.7	76.1	4.8	54.6	16.7
225	87.8	94.0	87.5	69.4	4.2	49.6	15.6
270	88.6	94.3	88.3	63.7	4.3	45.0	14.5

Note: D-content of molecular hydrogen in the feed equals 97.4%. Gas-collecting tube being switched on stream between 45 and 90 min.

n-octane conversion, which moderately decrease with time on stream. Starting with nearly zero values, the olefin formation slightly increases with time on stream while the formation of aromatics decreases (Table 1). The main products are C_8-aromatics, mostly saturated C_1–C_5 aliphatics (cracking products), and C_8 olefins. As pointed out in [4], the tracer concentration of the molecular hydrogen in the DHC product stream is declines from its feed value. This effect—the tracer dilution—can be caused by two reasons:

1. During the reaction, additional molecular hydrogen is produced from the D-free *n*-octane (tracer dilution by reaction).

2. The deuterium atoms of the molecular hydrogen are exchanged with the protium atoms of the reacting hydrocarbons by reversible dehydrogenation/hydrogenation steps of the DHC reaction (tracer dilution by exchange).

Calculating the possible "dilution by reaction" with the help of the hydrogen mass balance (olefin and aromatics formation accounted) and also the maximum "dilution by exchange" effects (all hydrogen of the reaction partners exchanging), one can compare these values with the experimental, and easily estimate the intensity of heteroexchange and, thus, of reversible dehydrogenation steps during DHC.

As demonstrated in Table 1, the tracer concentration of the molecular hydrogen in the product stream, calculated from the "dilution by reaction" (third column of Table 1), is significantly higher than the measured values (second column). These measured values are in good agreement with those calculated under the assumption of complete H–D exchange between molecular hydrogen and hydrocarbon products.

The corresponding tracer distribution within product gas components (aromatics, olefins, and not converted *n*-octane) is demonstrated in Fig. 3. Aromatics and olefins are highly deuterated with the distribution maxima reached at one H atom and, respectively, 9 and 15 D atoms per molecule. About 75% of the *n*-octane molecules remain free of the tracing element. Some 20% are marked with one or two D-atoms, and at 3–4 H atoms, we observe a flat distribution maximum. The cracking products are highly-deuterated.

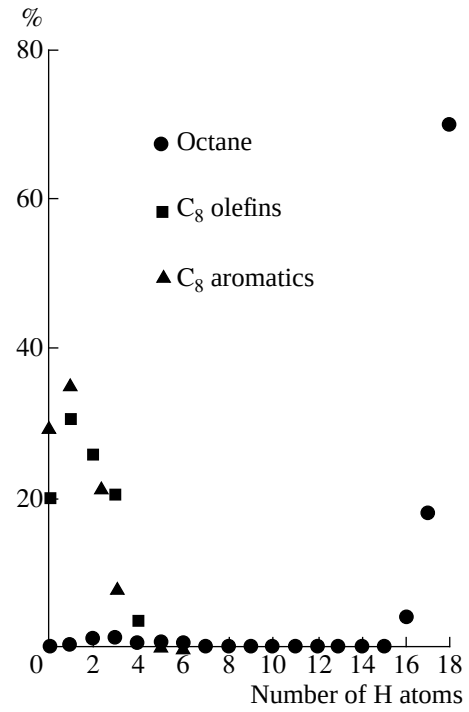

Fig. 3. Tracer distribution in hydrocarbons under low feed rate conditions.

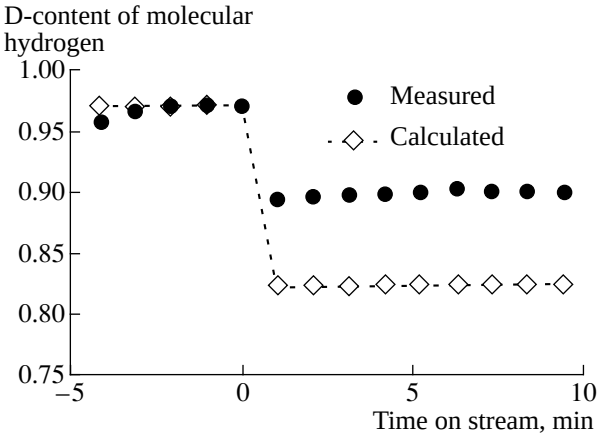

Fig. 4. H–D exchange between *o*-xylene and D-tracered molecular hydrogen: tracer dilution.

Further discussion of the tracer distribution within the hydrocarbons demands certain knowledge about distribution rules. In the case of our tracer experiments, one of the chemical elements (hydrogen, normally consisting of nearly pure protium) of certain chemical species being *n*-atomic with respect to this element (*n*-octane, *n*-octenes, and C_8 aromatics) gets marked by a tracer (deuterium). If this marking proceeded by a random process, then the tracer distribution within the marked molecules is binomial. The distribution coefficients equal the correspondent binomial row and can be calculated from

$$[\alpha + (1-\alpha)]^n = \sum_{i=0}^{n} \binom{n}{i} \alpha^{n-i}(1-\alpha)^i,$$

with α being the marked (deuterium) fraction and $(1-\alpha)$ the unmarked (protium) fraction of the marked element within the investigated chemical species.

With deuterium marked C_8 aromatics (containing 10 hydrogen atoms), we get the following equilibrium distribution of isotopic molecules:

$$[\alpha + (1-\alpha)]^{10} = \alpha^{10} + 10\alpha^9(1-\alpha) + 45\alpha^8(1-\alpha)^2 + 120\alpha^7(1-\alpha)^3 + 210\alpha^6(1-\alpha)^4 + 252\alpha^5(1-\alpha)^5 + 210\alpha^4(1-\alpha)^6 + 120\alpha^3(1-\alpha)^7 + 45\alpha^2(1-\alpha)^8 + 10\alpha(1-\alpha)^9 + (1-\alpha)^{10}.$$

At α values of 0.90, the C_8 aromatics tracer distribution maximum is reached at 1 H and 9 D atoms per molecule. In the case of C_8 olefins, the maximum is achieved at 1 H and 15 D atoms.

In the low feed rate experiments, this is in good agreement with the measured (Fig. 3) tracer distribution within the aromatics and olefins and indicates a tracer equilibration between these species and molecular hydrogen. The *n*-octane tracer distribution measured under these conditions seems to be more complex and will be discussed later.

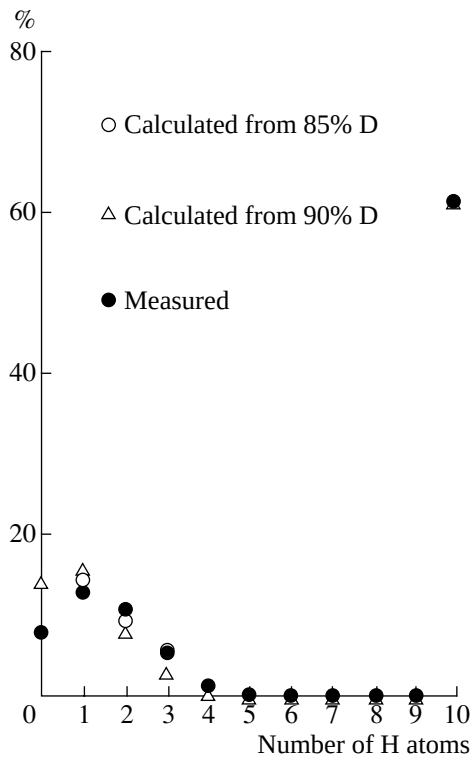

Fig. 5. H–D exchange of *o*-xylene and D-tracered molecular hydrogen: tracer distribution within *o*-xylene.

D_2/*o*-xylene exchange experiments immediately made after low feed rate DHC experiments at correspondent reaction conditions (*o*-xylene instead of *n*-octane) show no measurable conversion of the *o*-xylene but a considerable H–D exchange between molecular hydrogen and *o*-xylene. The measured tracer dilution (Fig. 4) in molecular hydrogen (α decreasing from 0.97 to 0.90) corresponds to partial heteroexchange between molecular hydrogen and *o*-xylene. Full exchange of the whole *o*-xylene would result in an α-value of about 0.82 (dotted line in Fig. 4).

The tracer distribution within the *o*-xylene molecules resulting from this experiment is shown in Fig. 5. The *o*-xylene clearly consists of two parts, one—about 60%—with 10 H atoms being not exchanged at all and the other part—about 40%—being highly exchanged with the D marked molecular hydrogen. The corresponding tracer distribution with a maximum at 1 H- and 9 D-atoms is very similar to that obtained in the low feed rate DHC experiment for the C_8-aromatics (Fig. 3) discussed above.

As seen from Fig. 5, the random tracer distribution calculated for the deuterated part of *o*-xylene using $\alpha = 0.85$ seems to fit better to the experimental data than the values calculated from $\alpha = 0.90$ measured in molecular hydrogen (Fig. 4). It seems likely that the molecular

Table 2. *n*-Octane DHC at 550°C with high feed rate: 750 mmol (g Cat)$^{-1}$ of D-tracered molecular hydrogen and 54.4 mmol (g Cat)$^{-1}$ of *n*-octane

Time	Tracer content of the molecular hydrogen in the product stream			Conversion			
	values measured	calculated without exchange	calculated with products exchange	of *n*-octane	to olefins	to aromatics	to cracking products
min	%	%	%	%	%	%	%
5	69.8	86.1	66.0	71.4	12.6	41.1	17.8
45	83.1	91.9	77.9	37.6	7.4	18.5	11.8
90	88.1	94.1	83.2	25.8	4.4	10.9	10.5

Note: D-content of molecular hydrogen in the feed equals 97.4%. Gas-collecting tube being switched on stream between 5 and 45 min.

hydrogen and the hydrogen of that part of *o*-xylene, which was adsorbed, underwent exchange during adsorption. The other part did not exchange at all.

The considerable amount of *o*-xylene remaining without any exchanged hydrogen correspond quite well to the rather low conversion of *n*-octane at the end of the preceding DHC experiment (see Table 1, Fig. 3) if we assume that slowly proceeding dissociative hydrocarbon adsorption is limiting both the *o*-xylene hydrogen-exchange

$$C_8H_{10} + 2Z \longrightarrow ZC_8H_9 + ZH$$

with Z symbolizing an adsorption center on the surface of the catalyst and that of *n*-octane DHC, too,

$$C_8H_{18} + 2Z \longrightarrow ZC_8H_{17} + ZH.$$

The latter concluded already by Shi and Davis [6] from their tracer investigations of *n*-octane DHC on Pt/Al_2O_3 and Pt/SiO_2 catalyst.

Our measurement of the tracer distribution in the *n*-octane remaining after reaction (Fig. 3) corresponds to this assumption: about 70% of the unconverted *n*-octane is not marked, because it did not take part in the reaction. 18% of the *n*-octane are single marked, 4% twice marked, and the remaining 8% show a flat distribution maximum at $C_8H_3D_{15}$. These distribution values at a conversion degree of about 93% mean that the formation of an olefin from *n*-octane is overwhelmingly irreversible. Once having dissociated, the probability of a ZC_8H_{17} dehydrogenating further to an adsorbed olefin equals about 98% and there is only about a 2% probability (30% of the unconverted 7% of the *n*-octane) of being hydrogenated to the paraffin. A certain part of the mentioned adsorbed species is formed by hydrogenation of highly deuterated olefins. Therefore, some percentage of the *n*-octane is highly deuterated, too.

Under low feed rate conditions, the amount of olefins in the product is very low. To get a higher olefin yield, we performed experiments with high feed rate. Results are shown in Table 2.

During sampling, the average tracer content of the molecular hydrogen in the product stream equals about 85%. Compared with the low feed rate experiments (Table 1), the C_8 olefins production is distinctly increased. Similar to the low feed rate experiment, the measured tracer dilution indicates an intensive H–D-exchange between molecular hydrogen and hydrocarbons. The measured tracer content of the molecular hydrogen in the product stream nearly equals the values calculated under assumption of complete H–D-exchange with the hydrocarbon products.

Under high feed rate conditions, the tracer distribution in the hydrocarbon product (Fig. 6) differs from that of low feed rate experiments. Aromatics show an equilibrium-like tracer distribution with a maximum at 2–3 H atoms corresponding to a tracer content of 75–80%, but the tracer content of the molecular hydrogen is somewhat higher (85%). Thus, under high feed rate conditions, the H–D exchange between hydrocarbons and molecular hydrogen is not complete. In the olefin fraction of the product, we observe a double maximum tracer distribution. This means that olefins must result from two sources. One of them is the "forward" way from the ZC_8H_{17} intermediate mentioned already. This part of the olefins is only poorly marked by deuterium (1–2 D atoms per molecule). The other source is the "backward" way via hydrogenation of polyene intermediates. This part is highly deuterated.

All results mentioned above correspond to a reaction scheme where the dehydrogenation steps between paraffins and aromatics are mostly reversible except the first. As we could not find any olefinic products in the D_2/*o*-xylene experiments, the mechanism must include additional irreversible steps. Such step could be, for instance, the ring formation.

$$C_8H_{18} + 2Z \longrightarrow ZC_8H_{17} + ZH$$
$$ZC_8H_{17} + Z \longleftrightarrow ZC_8H_{16} + ZH \longleftrightarrow C_8H_{16}\ \text{desorbed}$$
$$ZC_8H_{16} + Z \longleftrightarrow ZC_8H_{15} + ZH$$
$$\vdots$$
$$\downarrow\ \text{irreversible cyclization}$$
$$\vdots$$
$$ZC_8H_{11} + Z \longleftrightarrow ZC_8H_{10} + ZH \longrightarrow C_8H_{10}\ \text{desorbed}$$
$$C_8H_{10} + 2Z \longrightarrow ZC_8H_9 + ZH$$
$$ZC_8H_9 + Z \longleftrightarrow ZC_8H_8 + ZH$$
$$H_2 + 2Z \longleftrightarrow 2ZH$$

This mechanism scheme means that the tracer content of the product is equal to that of the surface hydrogen. With fast dissociation of molecular hydrogen (compared with the DHC rate), the tracer content of the surface hydrogen is mostly equal to that of the molecular hydrogen in the gas phase. Only at high feed rates could one expect the tracer content of the products to differ slightly from that of the gas phase hydrogen.

In previous work [4] we measured the dissociation rate of the molecular hydrogen under DHC conditions. With W = 10 mol H_2/(g Cat h), it is more than two orders of magnitude higher than the DHC rate value equaling 25 mmol *n*-octane/(g Cat h) (values measured after 5 min time on stream at 530°C with 114 mmol *n*-octane and 5 mol of molecular hydrogen per g catalyst and hour). Such rate proportion is in agreement with the small decline from tracer equilibration between molecular hydrogen and hydrocarbon products.

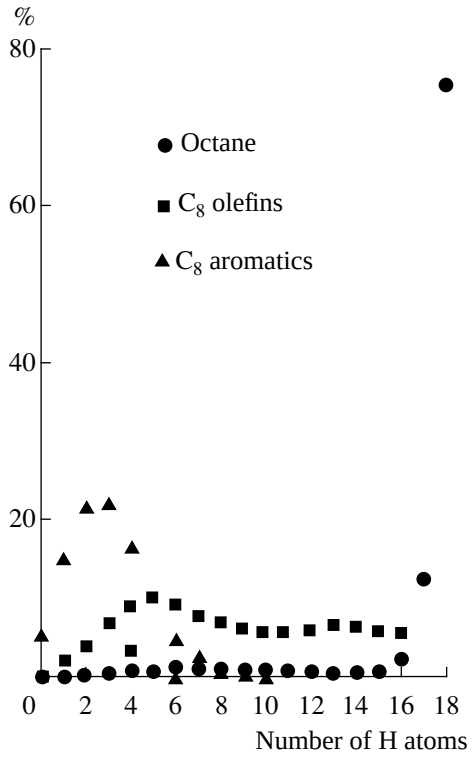

Fig. 6. Tracer distribution of hydrocarbons under high feed rate conditions.

Being highly deuterated, the short chain cracking products seem to result from side reactions of unsaturated DHC intermediates.

CONCLUSIONS

Investigations of the D tracer transfer between molecular hydrogen and hydrocarbon product components during standard DHC experiments allowed conclusions about the reversibility of hydrogenation/dehydrogenation steps to be formed. Similar to metal catalysts, the limiting step of DHC is the dissociative adsorption of the paraffin. Further dehydrogenation seems to be predominantly reversible.

ACKNOWLEDGMENTS

This work was supported by the Berlin Senat Department of Science, Research, and Culture (project no. 89-11-30001) as well as by the Federal Ministry of Education and Research of the Federal Republic of Germany (project no. 03C30120). The authors are grateful to MEL Chemicals, Manchester, UK, for supplying them with zirconia materials.

REFERENCES

1. Davis, B.H., *Catal. Today*, 1999, vol. 53, p. 443.
2. Shi, B. and Davis, B.H., *J. Catal.*, 1994, vol. 147, p. 38.
3. Ehwald, H., Hoang, D.L., Leibnitz, U., and Lieske, H., *Catal. Lett.*, 2000, vol. 70, p. 23.
4. Ehwald, H., Hoang, D.L., Leibnitz, U., and Lieske, H., *Stud. Surf. Sci. Catal.*, 2001, vol. 139, p. 117.
5. FRG Patent DE-OS 19612000.
6. Shi, B. and Davis, B.H., *J. Catal.*, 1997, vol. 168, p. 129.
7. Shi, B. and Davis, B.H., *J. Chromatogr.*, 1993, vol. 654, p. 319.
8. Shi, B., Keohg, R.A., and Davis, B.H., *J. Chromatogr.*, 1994, vol. 678, p. 94.