

Hydrogen/Deuterium Exchange during *n*-Butane Conversion on H-ZSM-5

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Steady-state isotope tracer studies and isotope transient response experiments of *n*-butane conversion on H-ZSM-5 (Si/Al = 35) were carried out between 673 and 823 K. Among the three main reactions, the rate of H/D-exchange is at least one order of magnitude higher compared to the rates of cracking or dehydrogenation. Its apparent energy of activation is lower than that of the latter two processes. The rates of H/D-exchange are higher for larger molecules than for smaller ones and faster with olefins than with paraffins. Proton exchange proceeds stepwise, i.e., only one hydrogen (deuterium) of the substrate is exchanged with one deuterium (hydrogen) in a single catalytic turnover. A kinetic isotope effect was found for protolytic cracking, but not for dehydrogenation. Protonation of the feed (deprotonation of the zeolite) is concluded to be involved in the rate determining step of cracking. © 1996 Academic Press, Inc.

INTRODUCTION

Steady-state and transient isotope tracing experiments were used in several studies to elucidate the mechanisms of catalytic reactions (1–16). The evaluation of the number and the position of the labeled molecules in the products (7, 12, 14) as well as the occurrence of isotope effects, i.e., the change in the corresponding rates (1–6, 9, 13, 16), permitted insight into the reaction pathways. Acid catalytic cracking and dehydrogenation of hydrocarbons involve steps in which C–H and O–H bonds are broken and formed (17–19). Thus, the rate at which the H/D-exchange occurs and the variations of the rates due to the isotopes involved are expected to yield information about the nature of the rate determining step(s).

Most work described in literature was carried out applying steady-state tracing techniques. Only few experiments (e.g., 2, 4) used isotope transient response techniques. *In situ* infrared spectroscopy and/or on-line mass spectrometry were the main tools for evaluating the isotope distributions on the catalyst surfaces or in the product molecules. For the conversion of linear alkanes, however, on-line mass spectrometry is difficult to apply, because the large number of similar products generates overlapping fragmentation patterns.

In the present communication we report transient response experiments in which the gas samples were first stored in the loops of multiposition valves and subsequently separated by gas chromatography. The separated products were analyzed using a mass spectrometer and a flame ionization detector. Additionally, *in situ* infrared experiments were carried out to assess the rate of H/D-exchange of the surface protons.

EXPERIMENTAL

H/D-exchange of *n*-butane and its reaction products on H-ZSM-5 was studied between 673 and 823 K by means of infrared spectroscopy and microkinetic experiments. H-ZSM-5 with a Si/Al ratio of 35, supplied by the Mobil Corp., was used. The concentration of Brønsted acid sites was 4.2×10^{-4} mol/g (20).

Kinetic Experiments

The catalytic experiments were carried out in a tubular flow reactor with an inner diameter of 5 mm operated under steady state and transient conditions between 733 and 813 K. Typical catalyst weights varied from 5 to 15 mg. The catalyst was activated in a stream of air by increasing the temperature with 5 K/min to 393 K and holding that temperature for 30 min. Then, the temperature was raised with 10 K/min to 853 K and kept at this level for 1 h. After activation, the catalyst was cooled to reaction temperature in He flow.

Perdeuterated *n*-butane was obtained from MSD Isotopes (isotopic purity 98.9%). Both *n*-(D₁₀)butane and *n*-(H₁₀)butane were used premixed in He (2% butane, 98% He). Krypton or argon (1000 ppm) was present in *n*-(H₁₀)butane. These gases were used to determine the transient response function of the reaction system. Flow rates were adjusted to values between 10 and 50 ml/min.

Pressure transient response experiments were carried out by switching from the carrier gas to a stream of He containing the reactant. Tubing (I.D. 0.25 mm) was kept as short as possible to minimize the dead volume in the system. Glass rods were inserted above and below the catalyst bed to

minimize the free volume in the reactor. At a volumetric flow rate of 30 ml/min the transient response time of the system was below 5 s.

The products were stored in multiposition valves and analyzed by means of gas chromatography using an $\text{Al}_2\text{O}_3/\text{KCl}$ capillary column linked to a flame ionization detector and a mass spectrometer. The absence of thermal cracking and/or hydrogen/deuterium exchange in the gas phase were confirmed by blank experiments. Diffusion limitations were absent as reported earlier (22). The absence of external transport resistance was confirmed by conversion/residence time studies; internal diffusion resistance was probed by varying the zeolite particle size between 0.5 and 30 μm . The calculation of the rates of product formation is described in Refs. 21 and 22. The evaluation of the deuterium content in the reactant and the products is described in detail in Ref. 22.

Infrared Spectroscopic Experiments

The kinetics of the H/D-exchange reaction (i.e., the time dependence of the effects of D_{10} -butane on the OH groups of H-ZSM-5) were investigated by means of *in situ* infrared spectroscopy. A continuous stirred tank reactor (CSTR) with IR transparent windows was used (volume of the reactor, 1.5 cm^3). The reactor was placed in the focus of the IR beam to monitor the catalyst during all treatments by means of time-resolved IR transmission absorption spectroscopy. Catalyst activation and transient response studies were carried out as described above for the kinetic measurements. The minimum time difference between two spectra was 15 s. n -(D_{10})butane exchanges the surface protons with deuterium atoms. After the exchange was complete, the reverse transient was carried out; i.e., the gas stream was switched back to n -(H_{10})butane in order to exchange the surface deuterium atoms back to protons. Then, the system was brought to the next desired temperature and reexchanged by n -(D_{10})butane. This was performed at 673, 723, 773, and 823 K. The overall conversion was below 1% at all temperatures. Under these conditions coke or hydrocarbon residues were not deposited on the zeolite.

RESULTS AND DISCUSSION

Isotope Transient Response Experiments

The results of the isotope transient response experiment at 773 K using a volumetric flow rate of 30 ml/min and a reactant pressure of 4 kPa are shown in Figs. 1–11. Figure 1 shows the response functions of the isotope selectivities (IS) for the butane molecules containing different amounts of H and D atoms. Before the step function was introduced to the reaction system, only n -(H_{10})butane entered and left the reactor. At $t = 0$ the n -(H_{10})butane feed was replaced by n -(D_{10})butane. The concentration of n -(H_{10})butane

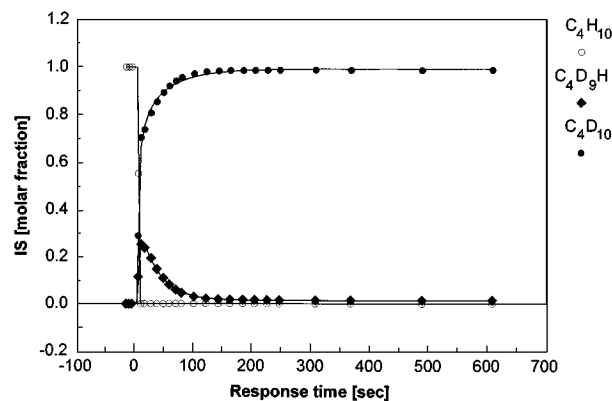


FIG. 1. Isotope selectivities of n -butane as a function of response time. (n -(H_{10})butane \rightarrow n -(D_{10})butane; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K)

decreased suddenly at a response time of approximately 5 s in parallel with the sudden decrease of the tracer gas (Kr). This time represents the time constant (τ_{sys}) of the reaction system. The shape of this decrease approximated a rectangle, indicating that the reaction system could be approximated by an ideal plug flow reactor.

At short response times some n -(D_9)butane was detected. The response curve of this species showed a maximum value at $t = \tau_{\text{sys}}$ and decreased toward higher response times. The concentration of this species reached zero after approximately 100 s. In contrast to the sudden decrease of n -(H_{10})butane, n -(D_{10})butane increased slowly in parallel with the decrease of n -(D_9)butane. The appearance of n -(D_9)butane in the products is attributed to the exchange of the deuterium atoms of n -(D_{10})butane with the surface protons of the catalyst.

n -Butane was converted to methane and propene, ethane and ethene, and the butene isomers. Additionally, small amounts of 1,3-butadiene were formed. Isobutane and propane, indicative for hydride transfer reactions, were not observed. The isotope selectivities of the differently labeled species of ethane as a function of response time are compiled in Fig. 2. The response functions of ethane were similar to those of n -butane. (H_6)Ethane decreased as fast as n -(H_{10})butane at $t = \tau_{\text{sys}}$. (D_6)Ethane increased in parallel with n -(D_{10})butane and (D_5)ethane decreased in parallel with n -(D_9)butane, suggesting weak interactions of ethane with the surface. Because ethane underwent little H/D-exchange, the fraction of deuterium atoms in ethane is concluded to be directly proportional to the fraction of deuterium present in n -butane.

Similarly, the concentrations of (H_6)propene and i -(H_8)butene decreased as fast as that of n -(H_{10})butane (Fig. 3). In contrast to the paraffinic products, however, the concentration of the perdeuterated olefins in the product gas stream increased with a slower rate (Fig. 4). The response functions of the molecules containing hydrogen and

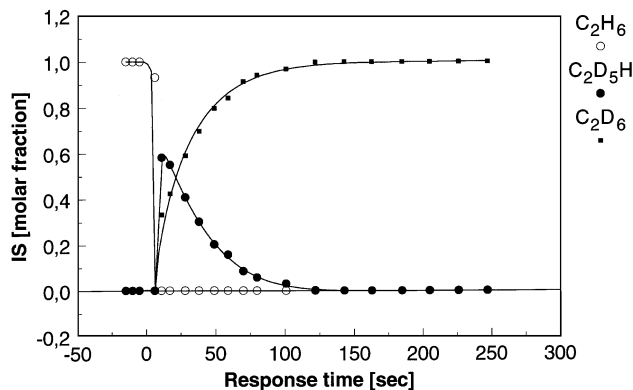


FIG. 2. Isotope selectivities of ethane as a function of response time. (n -(H_{10})butane \rightarrow n -(D_{10})butane; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K)

deuterium atoms proceeded through a maximum (Fig. 5). The response times of the maxima increased in parallel with the fraction of deuterium atoms in the product (i.e., $\tau(C_3H_5D)_{\text{max}} < \tau(C_3H_4D_2)_{\text{max}} < \dots < \tau(C_3H_1D_5)_{\text{max}} < \tau(C_3D_6)_{\text{max}}$). This indicates a stepwise exchange of the deuterium atoms of the hydrocarbons with the acid protons of the catalyst (Fig. 6).

The response times of the maxima increased in the sequence of increasing molecular weight. For a particular size of the molecule the response times of the maxima of the olefins exceeded those of the paraffins. In agreement with these observations, the response functions of the perdeuterated products increased in the same sequence (see Fig. 4) as the maxima for the molecules containing one hydrogen atom. The concentration of the nonlabeled products decreased, in contrast, at the same response times (i.e., at τ_{sys}), in parallel with the tracer gas (see Fig. 3). This indicates that the differences in the adsorption constants of products are too small to be observed under the experimental conditions used. Note, however, that upon using 600 mg of catalyst and

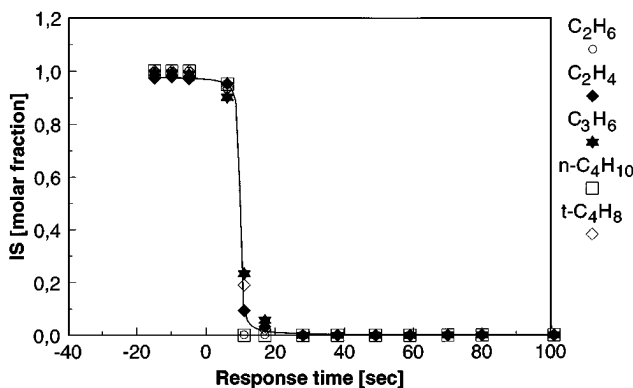


FIG. 3. Isotope selectivities of the products containing only hydrogen atoms as a function of response time. (n -(H_{10})butane \rightarrow n -(D_{10})butane; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K)

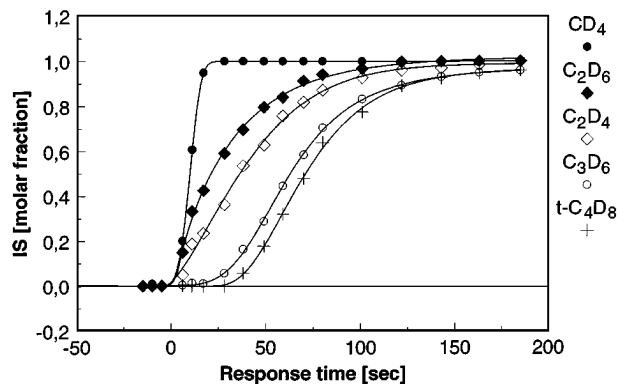


FIG. 4. Isotope selectivities of the perdeuterated products as a function of response time. (n -(H_{10})butane \rightarrow n -(D_{10})butane; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K)

a flow rate of 30 ml/min, significant differences in the retention of the various products were observed. Under these experimental conditions the larger and the unsaturated hydrocarbons reached steady state much later in the gas phase than the smaller or saturated products.

Figure 7 shows the deuterium content of the reactant and some reaction products as a function of the response time. At any time the deuterium distribution in the feed and in the product molecules could be described by a binomial distribution. The probabilities for a single exchange event were obtained by a least squares optimization. The so obtained probability for a given product at any response time was numerically identical to its deuterium content. Thus, the single exchange events are independent from each other. The deuterium concentrations in the different products at a given time reflect the differences in the number of interactions of these products with the catalyst surface. The reactivity of the paraffins and the olefins increased with increasing molecular weight. However, it was generally observed that the deuterium concentrations of propene and the butene

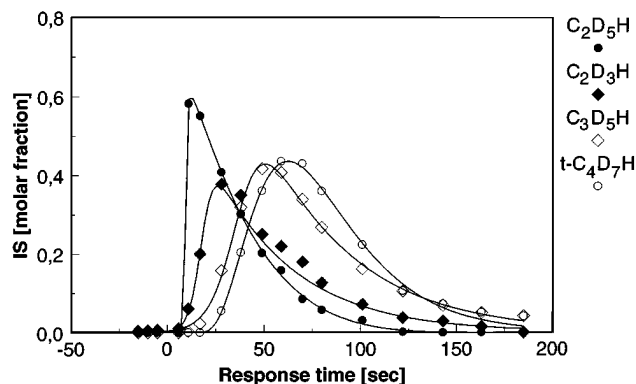


FIG. 5. Isotope selectivities of the products containing one hydrogen atom as a function of response time. (n -(H_{10})butane \rightarrow n -(D_{10})butane; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K)

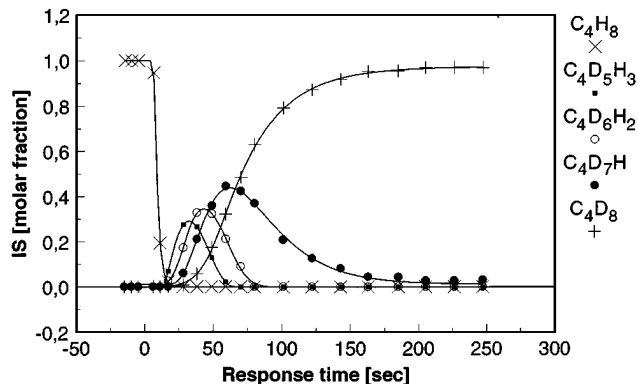


FIG. 6. Isotope selectivities of *i*-butene as a function of response time. D₁ to D₄ were omitted for the sake of clarity. (*n*-(H₁₀)butane → *n*-(D₁₀)butane; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K)

isomers were nearly identical; i.e., the deuterium concentration of propene was only slightly smaller than that of the butene isomers. Thus, we conclude that the deuterium concentrations in the butenes and in propene correspond to the total deuterium concentration of the catalyst surface.

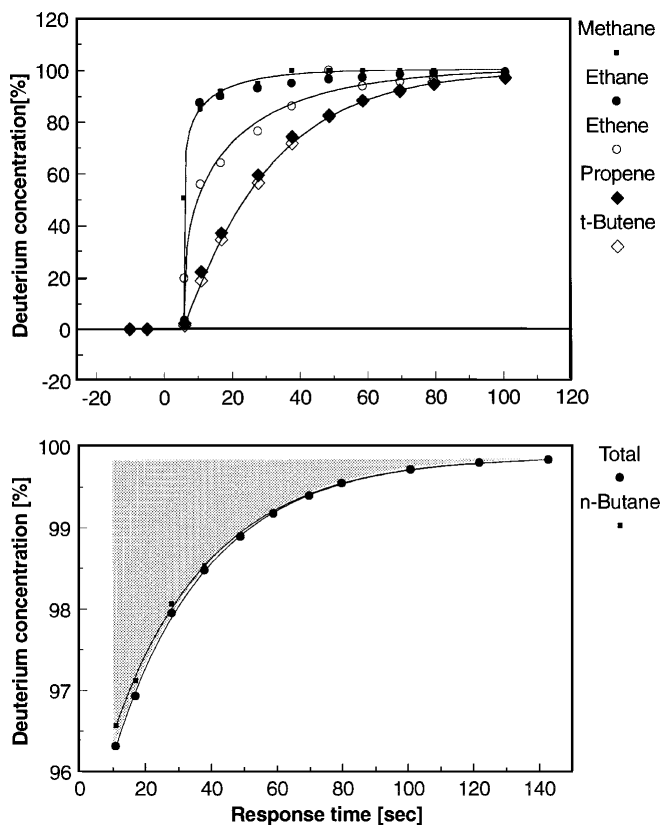


FIG. 7. Deuterium concentration in reactant and products as a function of response time. Amount of protons exchanged by *n*-(D₁₀)butane. (*n*-(H₁₀)butane → *n*-(D₁₀)butane; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K)

Propene and butene readsorb many times before they desorb from the catalyst and the H/D-exchange of these products is equilibrated.

These results clearly indicate different strength of interaction of the various product molecules with the catalyst surface. The concentration of protons in the product olefins is far higher compared to the paraffins at any response time during the transient period, indicating that the true residence time of these products with the surface is higher than that of the paraffins. The results agree well with the fact that the adsorption constants for unsaturated hydrocarbons (20) are significantly higher than for alkanes.

The Rate of H/D-Exchange

Figure 7 compiles the total deuterium concentration (in the feed and the products) as a function of the response time. The similar transient response of the deuterium concentration in butane and the total deuterium concentration indicates that a large fraction of the hydrogen atoms is exchanged by butane and not by the reaction products, although the interaction of the olefins is by far stronger than that of *n*-butane. This is attributed to the large difference in concentration between *n*-butane and the reaction products. (The overall conversion was approximately 2%.)

The gray shaded area above the butane response curve (see Fig. 7) multiplied by the molar feed approximates the number of surface protons exchanged during the transient period. This value was approximately equal to the concentration of Brønsted acid sites (4.2×10^{-4} mol/g) at all temperatures investigated, indicating that all OH groups were exchanged. The average exchange rate was calculated from the total number of exchanged surface protons and the time necessary to exchange all protons on the catalyst surface. The values obtained for 733, 773, and 813 K are compiled in Table 1. The rate of H/D-exchange was approximately one order of magnitude larger than the rates of cracking and dehydrogenation. The corresponding apparent energy of activation was determined to be 78 kJ/mol.

TABLE 1
Rates of H/D-Exchange and Protolytic Cracking and Dehydrogenation [mol/g s mbar]

<i>T</i> (K)	IR	SSITR initial	SSITR average	Cracking	Dehydrogenation
673	2.5×10^{-8}				
723	4.7×10^{-8}				
733		8×10^{-8}	4×10^{-8}	4.2×10^{-9}	1.7×10^{-9}
773	1.4×10^{-7}	1.7×10^{-7}	8.2×10^{-8}	7.3×10^{-9}	2.8×10^{-9}
813		2.8×10^{-7}	1.4×10^{-7}	2.1×10^{-8}	6.4×10^{-9}
823	3.3×10^{-7}			2.8×10^{-8}	7.9×10^{-9}
E_A [kJ/mol]	80	78	77	135	115

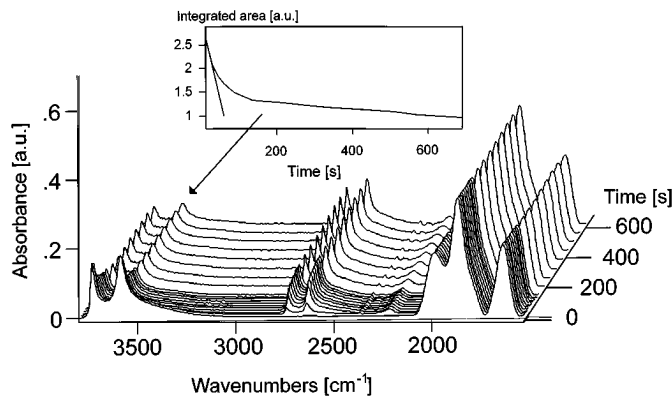


FIG. 8. Time resolved IR spectroscopic investigation of H/D-exchange on H-ZSM-5 at 773 K. (n -(H_{10})butane \rightarrow n -(D_{10})butane; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K)

As outlined above the deuterium concentration in the butene isomers reflects the deuterium concentration of the catalyst surface. Thus, the initial H/D-exchange rate was calculated from the time dependence of the deuterium concentration in the butenes (see Fig. 7). This rate was higher than the averaged H/D-exchange rate and agreed very well with the data obtained from the IR spectroscopic measurements described below. The corresponding apparent energy of activation was 77 kJ/mol.

Figure 8 shows the IR spectra of H-ZSM-5 as a function of time on stream in the presence of 2% n -(D_{10})-butane in He at 773 K. The spectrum at time zero, i.e., the sample without contact to n -(D_{10})-butane, exhibited bands at 3733 and 3583 cm^{-1} . These absorption bands are attributed to OH stretching vibrations of terminal SiOH groups (23, 24) and of SiOHA1 groups (25, 26), respectively. Bands at 1978, 1861, and 1629 cm^{-1} are attributed to overtones of the zeolite lattice vibrations. After the n -(D_{10})butane/He mixture was passed over the catalyst the bands assigned to the OH stretching vibrations decreased in intensity. New bands at 2746 and 2642 cm^{-1} appeared which were attributed to OD stretching vibrations.

The integral intensity of the band at 3583 cm^{-1} (SiOHA1 groups) versus time is plotted in the separate box in Fig. 8. The rates of HD exchange were calculated from the initial dependence of the OH concentration upon the contact time with n -(D_{10})butane. The values are compiled in Table 1. From measurements at various temperatures the apparent energy of activation for the H/D-exchange over H-ZSM-5 was determined to be 85 kJ/mol. The exchange of the terminal SiOH groups is attributed to the presence of trace amounts of water (4).

Isotope Effects

Figure 9 shows the rates of cracking and dehydrogenation as a function of the response time for the n -(H/D)butane transient described above. The rate of n -(H_{10})butane

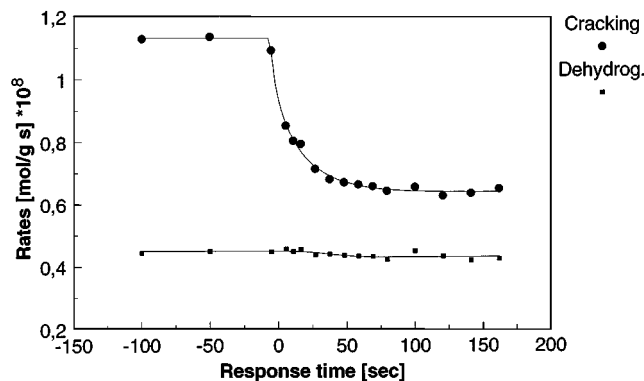


FIG. 9. Rates of cracking and dehydrogenation as a function of response time. (n -(H_{10})butane \rightarrow n -(D_{10})butane; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K)

cracking was 1.7 times higher than that of n -(D_{10})butane, indicating an appreciable isotope effect. Note that the rate of cracking decreased in parallel to the decreasing proton concentration on the catalyst surface, indicating that the O–H (O–D) bond cleavage, i.e., the protonation of the alkane (deprotonation of the zeolite), is most important for the rate determining step.

The results were confirmed by a step-up transient experiment (i.e., increasing the partial pressure of n -(H_{10})butane from 0 to 40 mbar) using a catalyst which only contained OD groups. The initial rate of cracking (surface covered with D, feed n -(H_{10})butane) was again 1.7 times lower than the rate obtained after the surface deuterium atoms were fully exchanged with the protons from the molecules. Because the ratios of the rates were found to be identical for the reactions, i.e.,

$$\frac{r(\text{C}_4\text{H}_{10} + \text{H}^*)}{r(\text{C}_4\text{H}_{10} + \text{D}^*)} = 1.7 = \frac{r(\text{C}_4\text{H}_{10} + \text{H}^*)}{r(\text{C}_4\text{H}_{10} + \text{D}^*)}, \quad [1]$$

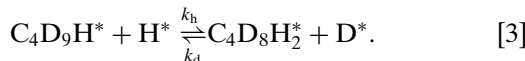
we conclude that it is primarily the cleavage of the OH bond of the zeolite or the proton addition (i.e., a kinetic isotope effect) which is responsible for the difference in the rates. Differences in the strength of reactant adsorption do not seem to play a role for the rate of the reaction.

In contrast to cracking, isotopic labeling of the feed or exchanging the surface protons with deuterium atoms hardly influenced the rate of dehydrogenation. Only a slightly lower rate was observed (factor 0.9–0.95) with n -(D_{10})butane. This suggests that protonation of the feed is not part of the rate determining step in dehydrogenation. It is speculated that the rate determining step for dehydrogenation should be close to product desorption.

Estimation of the Rate Constants for H/D-Exchange

The above-described reactions allowed us to conclude that the proton/deuterium exchange reaction proceeds stepwise. The forward and backward reactions for a single

exchange event are formulated in



The rate equation for the formation of, e.g., $\text{C}_4\text{H}_9\text{D}$, is given then by

$$\begin{aligned} r_{\text{C}_4\text{D}_9\text{H}} = & k_h \cdot [\text{C}_4\text{D}_{10}^*] \cdot [\text{H}^*] - 0.1 \cdot k_d \cdot [\text{C}_4\text{D}_9\text{H}^*] \cdot [\text{D}^*] \\ & - 0.9 \cdot k_h \cdot [\text{C}_4\text{D}_9\text{H}^*] \cdot [\text{H}^*] \\ & + 0.2 \cdot k_d \cdot [\text{C}_4\text{D}_8\text{H}_2^*] \cdot [\text{D}^*] \end{aligned} \quad [4]$$

In this way the rate of formation of every labeled species was defined. In all equations, a statistical factor (e.g., 0.1, 0.2, etc.) was introduced to account for the fact that the probabilities of exchange in the forward or backward direction vary with the deuterium content of the molecule. The resulting rate equations were combined with the mass balances of the components in the gas phase and at the surface (27):

$$V \cdot \frac{dc_i}{dt} = q^{\text{in}} \cdot c_i^{\text{in}} - q \cdot c_i + \sum_{j=1}^l m \cdot n_{ij} \cdot r_j \quad [5]$$

$$\frac{d(\Theta_j \cdot [\text{S}])}{dt} = \sum_{j=1}^l n_{ij} \cdot r_j \quad [6]$$

The resulting set of differential equations was integrated and the parameters optimized using SIMUSOLV. Figure 10 shows the experimental results for a H/D transient response experiment on H-ZSM-5 and the results of the optimization. The experimentally determined response curves of C_4D_{10} , $\text{C}_4\text{D}_9\text{H}$, and $\text{C}_4\text{D}_8\text{H}_2$ are well described by the values predicted from the model. The estimated rate constants

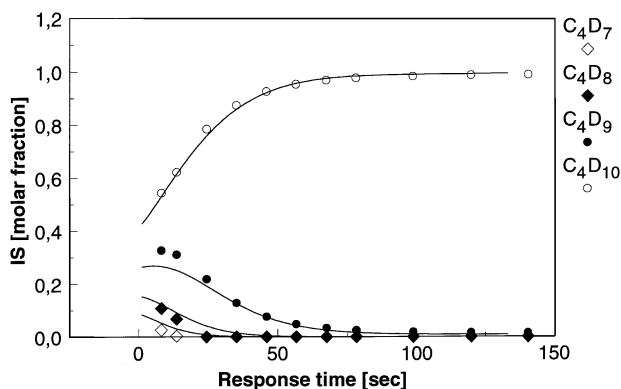


FIG. 10. Results of the parameter estimation. Experimentally observed isotope selectivities are represented by symbols, the calculated selectivities by lines. ($n\text{-(H}_{10}\text{)butane} \rightarrow n\text{-(D}_{10}\text{)butane}$; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K).

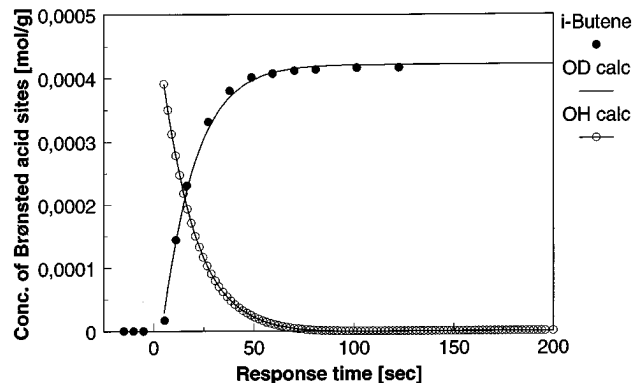


FIG. 11. Results of the parameter estimation. OH (OD-) concentrations (calculated) the deuterium content in *i*-butene (experimental) as a function of response time. ($n\text{-(H}_{10}\text{)butane} \rightarrow n\text{-(D}_{10}\text{)butane}$; H-ZSM-5, $p_{\text{butane}} = 4$ kPa; 773 K).

k_h and k_d were 0.042 and $0.017 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. The initial rate for the H/D-exchange was determined to be $2.5 \times 10^{-7} \text{ mol s}^{-1} \text{ g}^{-1} \text{ mbar}^{-1}$, which is in reasonably good agreement with the values obtained from the other methods.

Figure 11 shows the calculated fraction of surface protons (deuterium atoms) in comparison to the deuterium concentration of *i*-butene as a function of response time. It can be seen that both curves match well, confirming our earlier conclusion that H/D-exchange of the butene isomers is in equilibrium. Thus, the fraction of hydrogen (deuterium) in the butenes is a direct measure of the surface proton concentration.

CONCLUSIONS

Steady-state deuterium labeling studies and H/D transient response experiments showed that the rate of protonation (deprotonation of *n*-butane) is fast compared to the rates of cracking or dehydrogenation. The corresponding apparent energy of activation is lower (80 kJ/mol) than that of cracking (135 kJ/mol) and dehydrogenation (115 kJ/mol). The initial rates and the corresponding energies of activation obtained from IR spectroscopic and microcatalytic experiments are identical, indicating that acidic surface hydroxyl groups are the sites for H/D-exchange.

The rate of H/D-exchange is higher for olefins than for paraffins and it increases with increasing molecular weight. Thus, it is directly proportional to the concentration of the hydrocarbon in the ZSM-5 pores (which itself is directly proportional to the sorption constant). The rate of the interactions of butene and propene with the acid protons is so rapid that the deuterium concentration in these products reflects the deuterium concentration of the surface. Proton exchange proceeds stepwise; i.e., only one hydrogen (deuterium) of the substrate is exchanged with one deuterium

(hydrogen) in a single catalytic turnover. Then the molecule diffuses to the next acid site.

A kinetic isotope effect was found for cracking. The rate of *n*-butane cracking on a protonic surface was 1.7 times higher than on a surface containing deuterium atoms. However, isotopic labeling of the feed had no influence on the rate of cracking. Thus we conclude that the protonation of the feed plays a key role in the rate determining step of cracking. Protonation of the substrate (deprotonation of the zeolite), however, does not seem to play a role in the rate determining step of protolytic dehydrogenation.

APPENDIX: SYMBOLS

τ	(s)	Response time
τ_{sys}	(s)	System response time
r_j	(mol g ⁻¹ s ⁻¹)	Rate of the <i>j</i> th reaction
k_h	(m ³ mol ⁻¹ s ⁻¹)	Reaction rate constant of <i>n</i> -butane on a protonic surface
k_d	(m ³ mol ⁻¹ s ⁻¹)	Reaction rate constant of <i>n</i> -butane on a deuterated surface
V	(m ³)	Reactor volume
q^{in}	(m ³ s ⁻¹)	Volumetric inlet flow rate
q	(m ³ s ⁻¹)	Volumetric outlet flow rate
c_i^{in}	(mol m ⁻³)	Gas phase concentration of the <i>i</i> th compound in the inlet gas
c_i	(mol m ⁻³)	Gas phase concentration of the <i>i</i> th compound in the outlet gas
n_{ij}		Stoichiometric coefficient for the <i>i</i> th compound in the <i>j</i> th reaction
[S]	(mol g ⁻¹)	Concentration of Brønsted acid sites
The isotope selectivity (IS) is defined as		
		$IS_{\text{C}_x\text{H}_y\text{D}_{a-y}} = \frac{[\text{C}_x\text{H}_y\text{D}_{a-y}]}{\sum_y [\text{C}_x\text{H}_y\text{D}_{a-y}]}$
a		Number of hydrogen and deuterium atoms in a chemical compound

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