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Deactivation of Zeolite Catalysts by Coke Formation

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The deactivation of ZSM-5, -11, and -48 in the cracking of mixtures of hexane with resp. propylene and hexadiene was measured in an electrobalance, operated in a differential mode and connected with an on-line gas chromatograph. In this way the deactivation of both the cracking reaction and the coking reaction could be observed. The effect of coke is more pronounced on its own rate of formation than on the rate of the cracking reaction, except with ZSM-48. Differences between the behavior of the three catalysts can be related to their structural characteristics.

1. INTRODUCTION

Previous work concerning the effect of chemical and structural properties of zeolites on their deactivation by coke formation in the cracking of paraffins has been reviewed by Rollmann and Walsh (*1*) and by Derouane (*2*). In general only changes of conversion with respect to time were measured—i.e., there was no determination of the deactivating agent itself. The experiments were usually carried out in integral reactors, so that when coke was determined, only average values were obtained. The shortcomings of this approach were discussed by Froment (*3, 4*).

In the present work use was made of an electrobalance, connected with a gas chromatograph. The electrobalance was operated in a differential mode, to eliminate effects of bypassing and to measure point values of the rates. The equipment yields the coke content of the catalyst and the rate of reaction of a key feed component, hexane, both as a function of time. The coke content versus time data can be differentiated to yield the coking rate versus time, $r_C = f(t)$. Both the rate of cracking, r_H and the rate of coking, r_C, can be related to the coke content, which is the true deactivating agent. Therefore, the approach permits separating the effect of coke on the deactivation of the main reaction on one hand and on its own formation on the other hand. Indeed, when there are no diffusional limitations, $r_H/r_H^0 = \Phi_H$, the deactivation function for the cracking and $r_C/r_C^0 = \Phi_C$, the deactivation function for the coking, for which so far no information has been published in the literature. Thus additional insight into the effect of coke can be obtained.

Three types of zeolites were investigated, to provide insight into the effect of the structure of the zeolite on the deactivation: (1) ZSM-5, which possesses a three-dimensional pore network consisting of sinusoidal channels intersecting linear channels and four identical channel intersections per unit cell; (2) ZSM-11, which is also characterized (*5*) by a three-dimensional pore network, with only intersecting linear channels, thus having two intersections per unit cell comparable to those of ZSM-5 and two additional intersections about 30% larger in size; and (3) ZSM-48, which has a unidimensional pore structure.

2. CATALYSTS AND EXPERIMENTAL SETUP

2.A. *Catalyst Preparation, Characterization, and Pretreatment*

The catalysts were prepared as described previously (*6, 7*), with the aim of achieving

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nearly identical crystal sizes and aluminium content. ZSM-48 was synthesized using hexamethonium bromide (*8*).

Crystal sizes were evaluated by scanning electron microscopy. They were found to be in the range 1–5 μm for all catalysts. The Si/Al ratios were determined by proton induced X-ray and γ-ray emission (PIXE and PIGE), as described elsewhere (*9*). They were found to be 46.5, 43.2, and 62.1 for ZSM-5, ZSM-11, and ZSM-48, respectively.

The crystallinity and integrity of the zeolite materials were further verified by X-ray powder diffraction and *n*-hexane sorption. All materials were more than 95% crystalline and corresponded to the expected structures. The sorption capacities and rates were also as expected, indicating that the channels or pore mouths were not encumbered by (alumino)-silicate debris.

2.B. *Experimental Setup*

The experimental set up is shown in Fig. 1. The electrobalance yields $C_C = f(t)$. Care must be taken to account for the amount of adsorbed components. The rate of coking, $r_C(t)$, is obtained as the slope of this curve. The initial rate of coking, r_C^0, is the slope at $t = 0$, when $C_C = 0$. Nitrogen blanketing protected the balance from the hydrocarbons.

The partial pressures were obtained from on-line GC analysis. A 16-way valve, kept at 190°C, permits storage of the samples while the two GC's were still analyzing previous samples. In this way a complete deactivation curve was obtained with one sample of catalyst.

GC1 (Packard Becker) was equipped with an FID detector and a 30-m RSL 160 BP capillary column. The carrier gas was

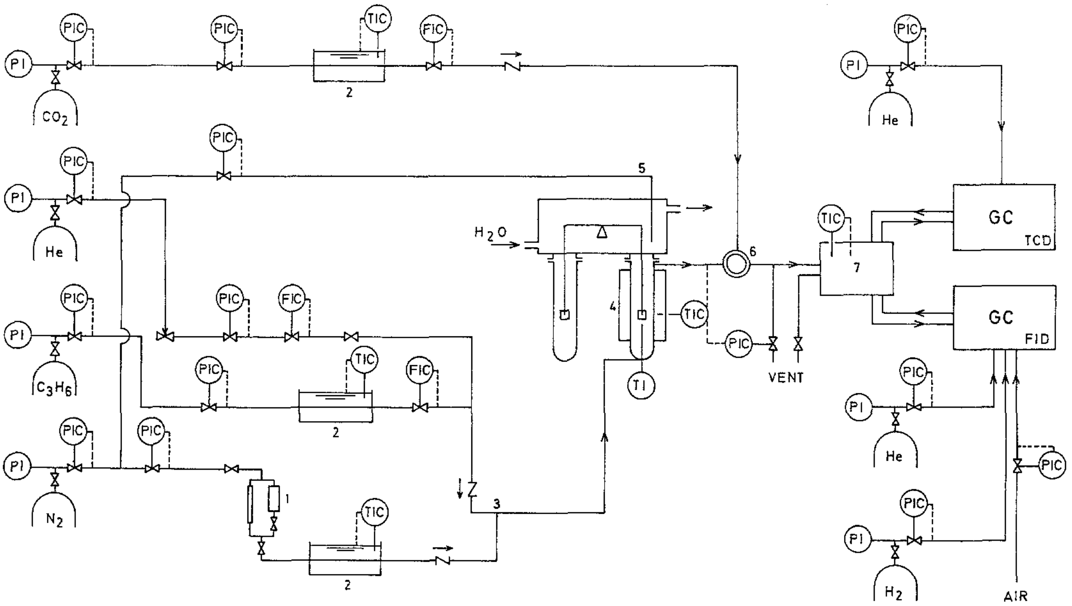

FIG. 1. (1) Reservoir for hexane (+ hexadiene) feed, under nitrogen pressure; (2) capillary in thermostat for flow measurement; (3) injection of hexane (+ hexadiene) in a flow consisting of He or He + propylene; (4) electrobalance differential reactor; (5) pressurization of balance chamber by means of nitrogen to avoid contamination by reacting gases; (6) cyclone for tar removal; injection of internal standard, CO_2; (7) 16-way gas sample storage valve from which samples are sequentially introduced into the gas chromatographs by means of the carrier gas flow.

helium. The temperature was programmed from −20 to 150°C and the components from methane up to xylene were detected.

GC2, containing a TCD detector, was operated with He as a carrier gas. The column was Porapack N, to separate N_2, CO_2, C_2H_4, and C_2H_6. This GC also contained a column for retaining the higher components.

An internal standard, CO_2, was injected after the electrobalance. This permitted an absolute analysis of C_2H_4 and C_2H_6, which were then used as secondary standards in the analysis on GC1. The carbon mass balances of the reported experiments deviated by less than 2%.

3. EXPERIMENTAL RESULTS

Operating the electrobalance in the differential mode with respect to hexane requires the conversion of the latter to be limited to low values. Under such conditions there is practically no carbon formation. Components responsible for carbon formation are olefins and diolefins, which are reaction products. With differential operation these products must be added to the feed to simulate conditions at a higher conversion. Since it is practically unfeasible to add all the products of the reaction, only two typical components were added: either propylene or hexadiene.

It was also verified for all cases that no temperature or partial pressure gradients occurred, so that the true deactivation functions Φ_A and Φ_C were obtained. For all the experiments the hydrocarbon partial pressure in the feed was 0.77 bar. The diluent was helium. Three temperatures were investigated: 460, 480, and 500°C.

3.A. Experiments with ZSM-5

3.A.a. Mixtures of n-hexane and propylene. Mixtures containing 0, 2.29, 4.36, 5.96, 7.88, and 10.0 mol% propylene were investigated. A total of 15 experiments was carried out, covering the three temperatures mentioned above. Figure 2 shows the rate of normal-hexane cracking as a function of the coke content of the catalyst, C_C, at various temperatures. This rate corresponds to the partial pressure of hexane in the feed, since the reactor is differential with respect to n-hexane conversion. The deactivation of the main reaction is negligible below a coke content of 3.5 wt%, in line with the observations of Kärger *et al.* on n-hexane cracking on ZSM-5 (*10*) and of Magnoux *et al.* on n-heptane cracking (*11*).

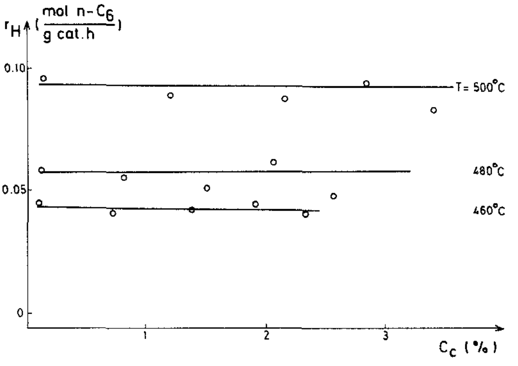

FIG. 2. ZSM-5. Rate of normal-hexane cracking as a function of coke content of catalysts. $W/F_H^0 = 0.304$ g cat h/mol nC_6; 9.998 mol% C_3H_6 in feed.

The shape selectivity of the catalyst, as sensed by the ratio of iso- to n-butane molar yields, is only weakly affected by the coke deposition, as shown in Fig. 3, because of the three-dimensional structure. The initial

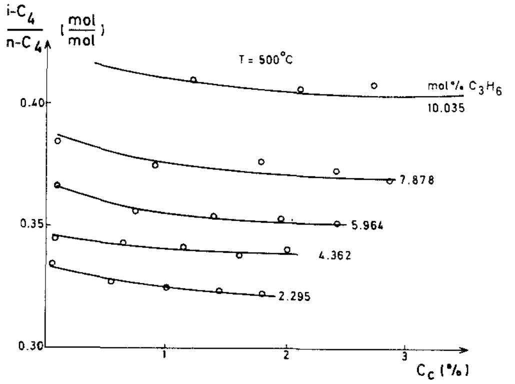

FIG. 3. ZSM-5. Ratio of iso- to normal-butane molar yields vs coke content. $W/F_H^0 = 0.304$.

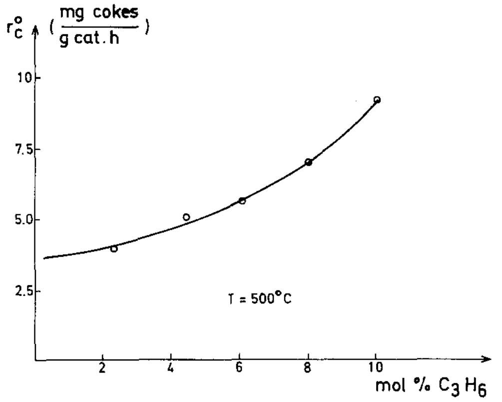

FIG. 4. ZSM-5. Initial coking rate vs propylene content of feed. $W/F_H^0 = 0.304$.

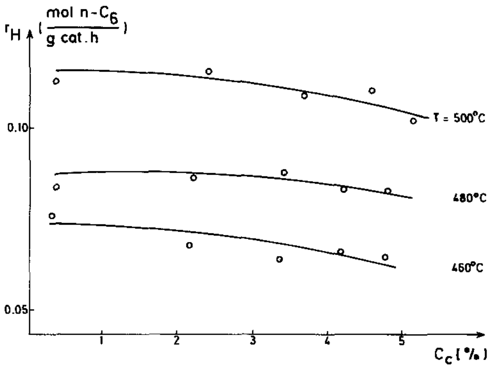

FIG. 6. ZSM-5. Rate of hexane cracking as a function of coke content. Mol% hexadiene in feed: 6.27. $W/F_H^0 = 0.304$.

coking rate at 500°C is plotted versus the propylene content of the feed in Fig. 4. The yield of aromatics also increases with the propylene partial pressure.

The deactivation function for the coking Φ_C is represented in Fig. 5, together with Φ_H, the deactivation function for the cracking. For a given temperature the relation Φ_C vs C_C is independent of the propylene content of the feed and linear, so that

$$\Phi_C = 1 - \alpha C_C.$$

By linear regression the following values were obtained for α: 21.8 at 500°C, 23.1 at 480°C, and 25.25 at 460°C, indicating a more pronounced effect of the carbonaceous residues at lower temperatures.

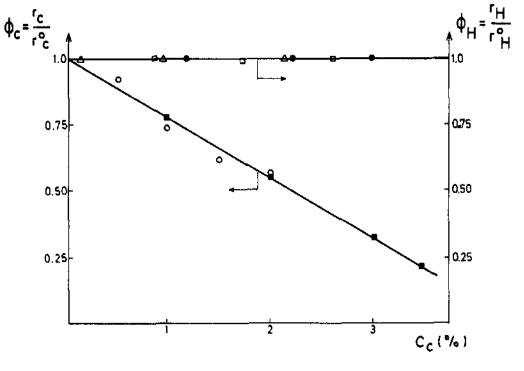

FIG. 5. ZSM-5. Deactivation function for coking. T = 500°C; $W/F_H^0 = 0.304$; (○) 4.18 mol% propylene in feed; (■) 10.05 mol%. Deactivation function for cracking. $W/F_H^0 = 0.304$; 9.998 mol% C_3H_6 in feed; (●) T = 500°C; (△) T = 480°C; (□) T = 460°C.

3.A.b. Mixtures of n-hexane and hexadiene. Six molar concentrations of hexadiene, ranging from 0.85 to 6.27 mol%, were investigated at 500, 480, and 460°C. Figure 6 shows the rate of cracking as a function of the coke content for a mol% of hexadiene in the feed of 6.27. The rates are higher than those observed in the presence of propylene.

The influence of the coke content on r_H is weak. At C_C = 5% the deactivation function for the cracking, Φ_H, still exceeds 0.90. For the given operating and feed conditions the selectivities for the various products are practically independent of the coke content, as shown in Table 1a. The ratio of the molar yields of *i*- to *n*-butane is also virtually unaffected by the coke content, as shown in Fig. 7. Figure 8 shows the initial rate of coking as a function of the hexadiene content. Coking is faster than with feeds containing propylene. For a same molar ratio with respect to *n*-hexane, hexadiene leads to more aromatics than does propylene.

The selectivity for aromatics at a molar content of 6.27% hexadiene in the feed is 8.68%, whereas with 10 mol% propylene it is only 2.94. On the same carbon number

TABLE 1a

ZSM-5: Selectivities for the Various Products as a Function of the Coke Content

C_C (%)	0.40	2.45	3.73	4.58	5.19
Methane	9.70	10.44	10.33	10.57	10.73
Ethylene	26.76	27.26	26.70	27.30	27.56
Ethane	14.30	14.67	14.62	14.84	14.97
Propylene	43.31	45.59	45.55	45.91	46.23
Propane	26.80	26.41	26.22	26.04	26.21
i-Butane	2.42	2.24	2.22	2.17	2.15
i- + 1-butene	13.95	14.31	14.20	14.27	15.10
n-Butane	6.63	6.40	6.35	6.26	6.28
t-But-2-ene	3.91	3.87	3.87	3.83	3.88
c-But-2-ene	2.92	2.89	2.87	2.87	2.89
i-Pentane	0.66	0.60	0.57	0.58	0.57
n-Pentane	1.10	1.06	1.05	1.01	1.04
C_5-olefins	7.50	7.70	7.67	7.69	7.58
Cyclopentane	0.94	0.92	0.89	0.87	0.92
2- + 3-Me-pentane	8.77	8.79	9.19	8.91	8.90
C_6-olefins	2.71	2.66	2.75	2.85	2.58
Me-cyclopentane	6.09	6.06	6.57	5.86	5.92
Benzene	2.22	1.83	1.91	1.95	2.00
Cyclohexane	0.66	0.76	0.75	0.74	0.84
C_7-paraffins	3.18	3.08	3.03	3.05	3.05
Toluene	3.04	3.19	3.14	3.23	3.30
Et-benzene	0.40	0.34	0.38	0.39	0.38
p- + *m*-Xylene	2.63	2.67	2.64	2.72	2.68
o-Xylene	0.52	0.52	0.51	0.52	0.52

Note. $T = 500°C$; $W/F_H^0 = 0.3038$ g cat h/mol; 6.267 mol% HD in feed; $p_{feed} = 0.77$ bar.

basis (feed composition corrected for molar percentage and chain length of coke precursor) the selectivity to aromatics of hexadiene should only be 3.68. Above a coke content of 3 wt% the aromatics content of the effluent is pronounced.

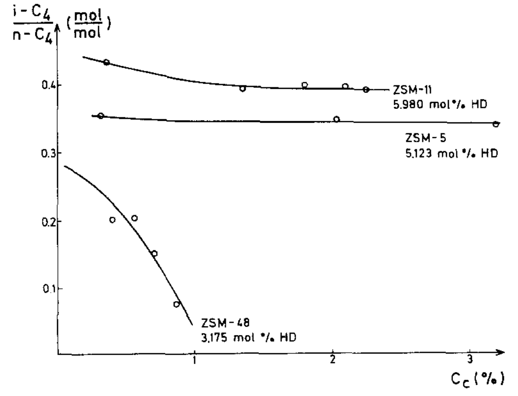

FIG. 7. ZSM-5. Iso- to normal-butane yield vs coke content for ZSM-5, -11, and -48 and hexane feeds containing hexadiene.

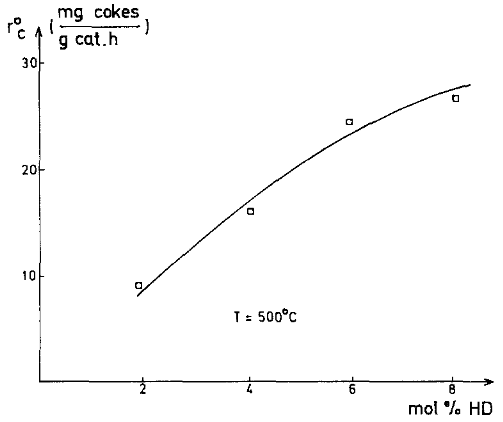

FIG. 8. ZSM-5. Initial rate of coking as a function of the hexadiene content of the feed. $W/F_H^0 = 0.36$.

The deactivation functions for the coking and for the cracking are represented in Fig. 9. The best fit is now obtained with $\Phi_C = \exp(-\alpha C_C)$, with $\alpha = 36.12$ at 500°C, 38.27 at 480°C, and 38.31 at 460°C, i.e., practically independent of temperature.

3.B. *Experiments with ZSM-11*

3.B.a. Mixtures of n-hexane and propylene. As for ZSM-5 the influence of the coke content on the rate of cracking of *n*-hexane is very weak. Because of the tridimensional channel network, the deactivation of the

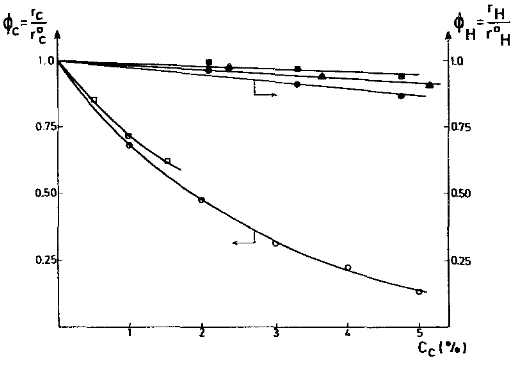

FIG. 9. ZSM-5. Deactivation function for coking. $T = 500°C$; $W/F_H^0 = 0.36$; (○) 0.85 mol% hexadiene in feed; (□) 5.167 mol%. Deactivation function for cracking. Mol% hexadiene in feed: 6.27; $W/F_H^0 = 0.36$; (●) $T = 460°C$; (■) $T = 480°C$; (▲) $T = 500°C$.

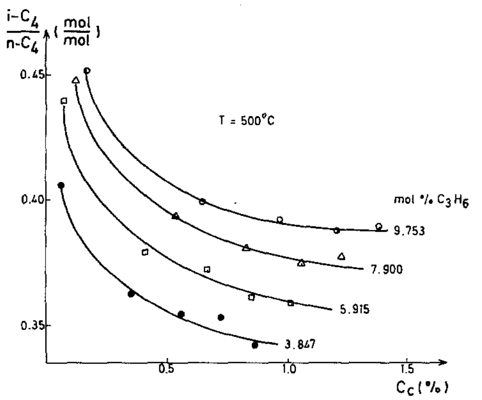

FIG. 10. ZSM-11. Iso- to normal-butane yield vs coke content. $W/F_H^0 = 0.36$. Feeds containing various propylene concentrations.

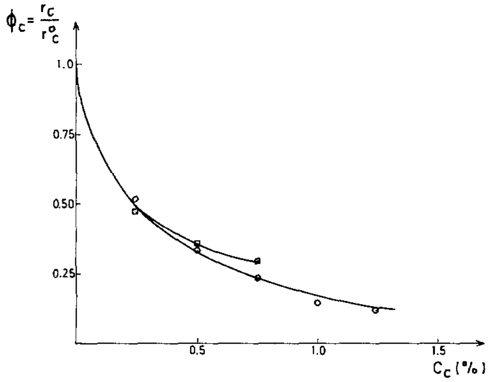

FIG. 11. ZSM-11. Deactivation function for coking. $T = 500°C$; $W/F_H^0 = 0.36$; (○) 9.753 mol% propylene in feed; (□) 3.847.

main reaction is not felt in the investigated C_C range. The influence of C_C on the iso- to normal-butane molar yields ratio is pronounced, as shown in Fig. 10. Also, the molar yield of *i*-butane is higher than that with H-ZSM-5, which is due to the larger size of some of the H-ZSM-11 channel intersections.

The ratio of *i*-/*n*-butane molar yields increases with the C_3H_6 mol%, as for H-ZSM-5 (Fig. 4). Again r_C^0 increases with the C_3H_6 mol% in the feed, but r_C^0 is approximately the same as that for H-ZSM-5. The selectivity for aromatics also increases with the C_3H_6 mol%. For the same coke content, the deactivation of the coking reaction is more important than that on H-ZSM-5. Figure 11 shows the deactivation function for the coking vs the coke content.

A hyperbolic law leads to the best fit. At 500°C:

$$\Phi_C = \frac{1}{1 + 412\, C_C},$$

but α_C is really a weak function of the C_3H_6 mol% in the feed, evolving from 340 to 508 as the C_3H_6 mol% varies from 3.8 to 9.7%.

3.B.b. Mixtures of n-hexane and hexadiene. Again the influence of the coke content on the rate of cracking of *n*-hexane is not very pronounced, as evidenced by Fig. 12, but also by Fig. 13. Table 1b illustrates that for given feed and operating conditions the selectivities do not vary with the coke content. They are close to those observed with ZSM-5. An insight into the shape selectivity variation with increasing C_C is obtained from Fig. 7.

The decrease in the *i*-/*n*-butane molar yields ratio is weaker than that with C_3H_6 addition. Again the ratio is higher when the percentage hexadiene is increased. Whereas the deactivation of the main reaction is weak, the deactivation function for the coking reaction, Φ_C, drops rapidly with increasing C_C, as shown in Fig. 13, and

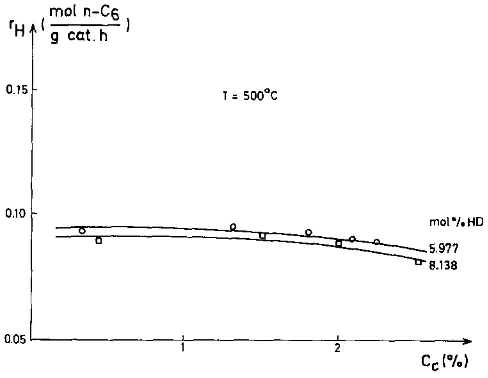

FIG. 12. ZSM-11. Rate of cracking of hexane vs coke content. $W/F_H^0 = 0.36$.

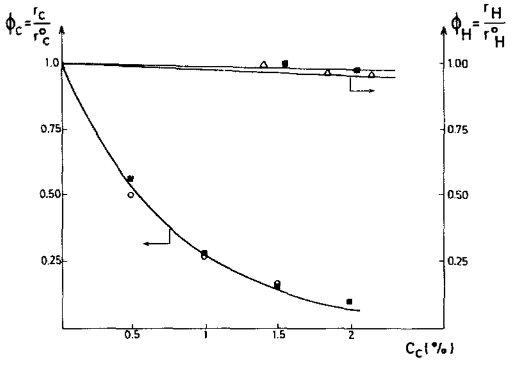

FIG. 13. ZSM-11. Deactivation function for coking vs coke content. T = 500°C; W/F_H^0 = 0.36; (○) 1.972 mol% hexadiene in feed; (■) 8.139 mol%. Deactivation function for cracking. T = 500°C; W/F_H^0 = 0.36; (△) 5.977 mol% HD in feed; (■) 8.139 mol%.

faster than for ZSM-5. When plotted vs C_C, the deactivation function Φ_C is independent of the hexadiene content of the feed. The effect of coke is less pronounced than with C_3H_6 addition.

TABLE 1b

ZSM-11: Selectivities for the Various Products as a Function of the Coke Content

C_C (%)	0.35	1.35	1.82	2.11	2.28
Methane	9.25	9.66	9.48	9.78	9.45
Ethylene	25.19	25.50	25.33	25.74	25.35
Ethane	14.24	14.37	14.42	14.57	14.34
Propylene	45.96	45.66	45.79	46.24	46.08
Propane	29.15	28.76	28.44	28.71	28.64
i-Butane	3.30	2.92	2.90	2.90	2.86
i- + 1-butene	13.40	13.63	13.53	13.63	13.69
n-Butane	7.64	7.40	7.32	7.38	7.34
t-But-2-ene	3.96	3.90	3.88	3.92	3.93
c-But-2-ene	2.97	2.93	2.93	2.92	2.93
i-Pentane	0.84	0.72	0.71	0.71	0.70
n-Pentane	1.23	1.22	1.18	1.22	1.17
C_5-olefins	7.14	7.30	7.25	7.34	7.35
Cyclopentane	1.26	1.19	1.26	1.24	1.23
2- + 3-Me-pentane	7.75	7.61	7.63	7.47	7.81
C_6-olefins	2.15	2.41	2.32	2.46	2.18
Me-cyclopentane	3.94	4.03	3.79	3.46	3.64
Benzene	2.00	1.88	1.93	2.00	2.27
Cyclohexane	0.67	0.78	0.69	0.79	0.78
C_7-paraffins	2.95	2.77	3.04	3.13	3.16
Toluene	2.88	2.95	3.46	2.99	2.95
Et-benzene	0.36	0.42	0.40	0.36	0.37
p- + *m*-Xylene	2.26	2.42	2.30	2.33	2.29
o-Xylene	0.61	0.59	0.57	0.54	0.57

Note. T = 500°C; W/F_H^0 = 0.3611 g cat h/mol; 5.997 mol% HD in feed; p_{feed} = 0.77 bar.

3.C. Experiments with ZSM-48

With this catalyst only mixtures of normal-hexane and hexadiene were investigated. The catalyst was less active for both cracking and coking than ZSM-5 and -11. As shown in Fig. 14, increasing the hexadiene content of the feed lowers the rate of cracking and this rate is significantly affected by the coke content, even at C_C values below 1%. This is evidently caused by the one-dimensional structure of ZSM-48. The deactivation function for the cracking is shown in Fig. 15. It is of the exponential type, typical for pore blockage, [Beeckman and Froment (*15*)]. The curve has been drawn for α_H = 108.5, an average of the α_H-values ranging from 108 to 109.7 for a hexadiene content in the feed varying from 1.34 to 3.89 mol%. The selectivities for the various products are shown in Table 1c. They differ markedly from those observed with ZSM-5 and ZSM-11. Also, during the same experiment the selectivities evolve as the coke content increases.

The effect of shape selectivity is again illustrated in Fig. 7, showing the evolution of the *i*-/*n*-butane molar yields ratio with respect to C_C. This ratio strongly decreases with increasing C_C. For a one-dimensional pore system this is an indication of pore mouth restriction and plugging, which is in contrast with ZSM-5 and -11. The 2- and 3-

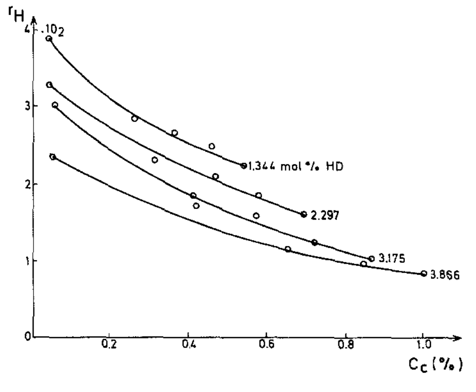

FIG. 14. ZSM-48. Rate of cracking of hexane vs coke content. T = 500°C; W/F_H^0 = 0.603.

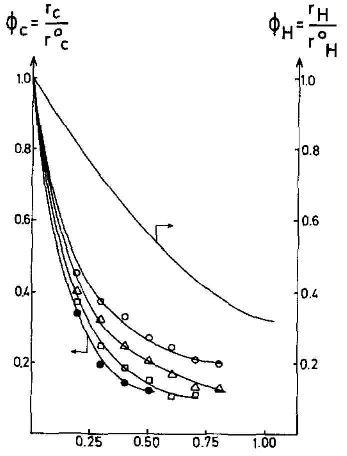

FIG. 15. ZSM-48. Deactivation functions for hexane cracking and for coking vs coke content. $T = 500°C$; $W/F^0_H = 0.602$; (○) 3.866 mol% hexadiene in feed; (△) 3.175; (□) 2.297; (●) 1.344.

methylpentane selectivity is twice as high as that with ZSM-5 and ZSM-11 and increases significantly with the coke content.

Further indicators of the pore restriction are the selectivities for benzene, toluene, and xylene, which vary significantly with the coke content for the same, very low hexane conversion: the benzene selectivity increases from 4.05 to 11.35%, the toluene selectivity decreases from 3.80 to 1.15%, the xylene selectivity from 2.60 to 1.00%, and the ethylbenzene selectivity from 0.44 to 0.07%. The more bulky toluene and xylene cannot escape as easily as benzene and are dealkylated, but ring formation leading to polyaromatics and coke is also likely. Yet, the total aromatics selectivity increases from 10.90 to 13.55%.

Note also the pronounced drop in propane and butane selectivity and the increase in the selectivity for C_5- and C_6-olefins. The rate of coke formation increases with the hexadiene content of the feed but the effect of coke becomes smaller, as is shown in Fig. 15, possibly because of a shift in the nature of the coke, associated with the shift in the selectivities reported in Table 1c.

The deactivation function Φ_C is also plotted vs C_C in Fig. 15 and Φ_C is lower for low HD contents. There is a pronounced influence of the hexadiene content of the feed. The best fit of Φ_C vs C_C is obtained with the hyperbolic function

$$\Phi_C = (1 + \alpha_C C_C)^{-1},$$

with $\Phi_C = f(\text{HD})$, again indicating pore blockage.

4. DISCUSSION

The present experiments not only provide information on the cracking reaction and the coke formation, but also on their respective deactivation.

The cracking reaction is practically unaffected by the coke formation with ZSM-5 and ZSM-11. A rapid deactivation is experienced with ZSM-48 and the deactivation function Φ_H decreases exponentially with the coke content, C_C. In ZSM-5 and ZSM-11 the carbonaceous residue is probably

TABLE 1c

ZSM-48: Selectivities for the Various Products as a Function of the Coke Content

C_C (%)	0.053	0.413	0.678	0.858	1.044
Methane	13.19	17.73	19.32	20.80	21.97
Ethylene	26.80	27.84	28.49	29.04	29.72
Ethane	13.35	13.56	13.24	13.12	13.93
Propylene	46.99	43.35	41.47	39.93	44.55
Propane	20.44	9.34	6.71	5.39	0.00
i-Butane	1.26	0.35	0.17	0.00	0.00
i- + 1-butene	14.39	16.04	17.00	16.95	17.61
n-Butane	4.49	1.80	0.93	0.70	0.51
t-But-2-ene	3.26	2.47	2.03	1.81	1.56
c-But-2-ene	2.46	1.79	1.55	1.33	1.13
i-Pentane	0.15	0.04	0.07	0.06	0.10
n-Pentane	0.86	0.50	0.51	0.46	0.60
C_5-olefins	7.48	8.69	9.34	9.09	9.59
Cyclopentane	1.48	1.76	2.02	1.94	2.45
2- + 3-Me-pentane	15.05	20.13	22.53	24.67	25.48
C_6-olefins	2.61	3.76	4.32	4.34	4.34
Me-cyclopentane	5.65	8.66	8.90	10.18	9.87
Benzene	4.05	6.42	8.41	10.81	11.34
Cyclohexane	0.97	1.09	1.20	2.25	2.97
C_7-paraffins	4.24	5.68	7.09	4.80	5.20
Toluene	3.79	3.34	2.54	1.84	1.14
Et-benzene	0.44	0.42	0.39	0.25	0.07
p- + *m*-Xylene	2.53	1.99	1.73	1.31	0.98
o-Xylene	0.09	0.08	0.12	0.16	0.02

Note. $T = 500°C$; $W/F^0_H = 0.6107$ g cat h/mol; 3.866 mol% HD in feed; $p_{\text{feed}} = 0.768$ bar.

formed at the intersection of the channels and at the surface, but it apparently still leaves a passage for *n*-hexane molecules, so that the cracking is practically not affected. With the one-dimensional structure of ZSM-48, blockage of the pores in two locations renders the active sites between the blockages inaccessible.

The variation in the *i*-/*n*-butane molar yields ratio with the coke content for the three catalysts can be related to the same effect. The coking reaction is significantly affected by the coke formation. In the case of ZSM-5 the deactivation function Φ_C varies linearly with C_C when propylene is added to the feed, which could indicate deactivation by site coverage. When hexadiene is added to the feed, the curve is nonlinear, which could indicate pore blockage, most likely at the intersections.

With ZSM-11 the deactivation function $\Phi_C = f(C_C)$ is nonlinear for both propylene and butadiene addition. At the same coke content the deactivation of the coking reaction is more pronounced with ZSM-11 than with ZSM-5. In ZSM-5 the deactivation function Φ_C in the presence of propylene is close to Φ_C in the presence of hexadiene, whereas these functions differ between themselves in ZSM-11. The channel intersections in ZSM-5 can contain roughly two molecules of propylene, which ultimately yields aromatics, very much in the same way as hexadiene. The channel intersections in ZSM-11 can contain up to three molecules of propylene. Alkylation leading to bulky aromatics then becomes more likely. However, only two molecules of hexadiene fit into the channel intersections, so that not only the two Φ_C are different, but also $\Phi_C(\mathrm{HD}) > \Phi_C(\mathrm{Prop})$ on ZSM-11. Also, $\Phi_C(\mathrm{HD})$ must be very close for both ZSM-5 and 11.

With ZSM-48 the blockage of the unidimensional structure also leads to a rapid decrease in Φ_C, which is less pronounced when the HD content of the feed is high. This is interpreted in terms of differences in the nature of the coke, accentuated by varying the hexadiene partial pressure. The significant shifts in selectivities observed with this catalyst may be an indication of this, but confirmation would require investigations of the mechanisms and kinetics of the coke formation.

5. CONCLUSION

This paper quantitatively and systematically confirms the influence of the structure of the zeolite on the deactivation of zeolites. The technique whereby an electrobalance is used as a differential reactor and is coupled with on-line gas chromatography permitted the definition of two deactivation functions: one for the cracking and one for the deactivation itself. The coking reaction is affected much more than the main reaction and reveals more about the influence of the structure of the zeolite than the deactivation of the main reaction.

APPENDIX: NOMENCLATURE

A	frequency factor	kmol/kg cat hr bar
C_C	coke content of catalyst	kg coke/kg cat
k	rate coefficient	kmol/kg cat hr bar
K	equilibrium constant	bar^{-1}
p_H	partial pressure of hexane	bar
p_p	partial pressure of propylene	bar
r_C	rate of coke formation	kg coke/kg cat hr
r_H	rate of hexane cracking	kmol/kg cat hr
Φ_C	deactivation function for coking	
Φ_H	deactivation function for cracking	
α	deactivation constant	kg cat/kg coke

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