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Effects of Coking on the Transport Properties of H-Mordenite[1]

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An experimental study of the relationships between coke content, catalyst activity, and intraparticle diffusivity is reported for cumene cracking on a commercial H-mordenite. Coking conditions were varied from 230 to 350°C at space velocities from 0.20 to 0.65 wt/hr/wt and time on stream up to 6 hr. Effective diffusivities of the catalysts were found to decrease by over a factor of 2 during the coking process and are nonlinearly related to the coke level, independent of the temperature of coking. Under conditions of strong diffusion limitation, this change in diffusivity alters the catalytic effectiveness in proportion to the square root of the diffusivity ratio, $(D_{\mathrm{eff}}/D^0_{\mathrm{eff}})^{1/2}$.

NOMENCLATURE

A	constant in Eq. (2)
a	constant in Voorhies correlation, Eq. (4)
B	constant in Eq. (2)
C	constant in Eq. (2), defined by Eq. (3)
C_c	coke content, wt%
C_0	concentration of cumene, moles/cm^3
D^0_{eff}	effective diffusivity of uncoked catalyst
D_{eff}	effective diffusivity of coked catalyst
D_{I}	diffusivity of tracer in chromatograph carrier, cm^2/sec
D_p	particle diameter, cm
F_{I}	void fraction of packed chromatographic column
F_{II}	$(1 - F_{\mathrm{I}})$
HETP	height equivalent of a theoretical plate, Eq. (1)
ΔH	heat of reaction (cal/mole)
K	distribution coefficient defined by Eq. (3a)
K_{eff}	effective thermal conductivity (cal/cm-sec-°C)
k	rate constant
L	length of packed chromatographic column (cm)
n	exponent in Voorhies correlation, Eq. (4)
R_s	spherical particle radius (cm)
r_v	volumetric rate of reaction (moles/sec-cm^3 catalyst)
T	temperature (°C)
T_p	catalyst pretreatment temperature (°C)
T_R	reaction temperature (°C)
t_e	retention time of the leading edge of tracer elution curve at 0.368 of maximum height (sec)
t_m	retention time of elution curve maximum (sec)

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t_0	retention time for nonadsorbable material at maximum of elution (sec)
u	interstitial velocity of carrier gas (cm/sec)
W_e	elution curve width at 0.368 maximum height (sec)
β	adsorption equilibrium constant for tracer
ϵ	pellet porosity
η	effectiveness factor determined for actual effective diffusivity
η^0	effectiveness factor determined for fresh catalyst effective diffusivity
θ	time on stream (hr)
Φ_s	modulus defined by Eq. (5)
ψ	Thiele modulus

INTRODUCTION

The question of the effect of coke deposition on the transport properties, in particular the diffusivity, of a catalyst has been studied by a number of workers, who report a wide range of results. Ozawa and Bischoff (*1*) report no change in either surface area or diffusivity of a commercial silica–alumina on coking by ethylene cracking (350–500°C, 1 atm) at coke levels of about 0.5 wt%. On the other hand, Appleby, Gibson and Good (*2*) report reductions on the order of 25% in surface area of a silica–alumina used for *n*-butene or phenanthrene cracking (500°C, 1 atm). Other conflicting studies involving cracking reactions are those of Ramser and Hill (*3*), who found a 27% decrease in surface on formation of 2.2 wt% coke, and Haldeman and Botty (*4*), who found very little effect of coke deposit on surface area at levels of several weight percent coke. Levinter, Panchekov and Tanatarov (*5*) report a striking series of experiments on silica–alumina catalysts demonstrating adsorption hindrance by pore mouth blockage due to coking. Finally, Tan and Fuller (*6*) found it necessary to assume a linear dependence of effective diffusivity on coke level in order to fit their experimental data on fouling of Y zeolite in benzene alkylation, while Suga *et al.* (*7*) report a linear decrease in diffusivity on coking of chromia–alumina in *n*-butane dehydrogenation (550°C, 1 atm).

Apparently, only Ozawa and Bischoff (*1*) and Suga *et al.* (*7*) have made direct measurements of diffusivity as a function of coke level; the conclusions of most workers have been based on inferences from surface area measurements. Further, with the exception of Tan and Fuller (*6*), no information of this nature pertaining to zeolites has been reported.

Eberly and Kimberlin (*8*) have measured the effective diffusivities of several types of uncoked mordenite catalysts, using a chromatographic procedure (*9*), and also report data on coking deactivation of these catalysts by cumene cracking in the range of 250–350°C. In the present study we have used the reaction and conditions of Eberly and Kimberlin to investigate the change in effective diffusivity with coke level for a commercial H-mordenite.

EXPERIMENTAL METHODS

The H-mordenite, either in the form of 2 × 6 mm cylindrical extrudates or 12–16 mesh irregular particles, was coked by cumene cracking in a small fixed bed reactor. Space velocity was varied from 0.20 to 0.65 g/hr/g, and reaction temperatures of 230, 260, 300 and 350°C were investigated.

The cumene used in the experiments was reagent grade, supplied by Eastman Organic Chemicals, and was purified by the method of Prater and Lago (*10*) to remove any hydroperoxide present. Helium, used as carrier gas in both the reactor and chromatograph, was Linde high purity grade and was used as supplied after passage through a drying train. Sulfur hexafluoride, employed as the tracer for measurement of diffusivity, was Matheson CP

TABLE 1
PROPERTIES OF THE CATALYST

Effective Intracrystalline Pore Diameter:	8–9 (Å)
Pellet density	1.24 (g/cm^3)
Porosity	0.34
Surface area (uncoked)	450 (m^2/g)

grade, and was used as supplied. The catalyst was Norton Zeolon 900H hydrogen form synthetic mordenite, supplied as self-bonded $\frac{1}{16}$ in. extrudates, which were segregated or sieved to the two size ranges employed in the experimentation. Some properties of this catalyst are given in Table 1.

In the coking experiments a series of runs up to several hours in duration was made at each temperature and space velocity. Catalyst was pretreated by maintaining the charge (normally about 3 g) under a helium flow of 50 cm^3/min overnight either at 260 or 350°C. The weight of pretreated catalyst was determined, with care to prevent adsorption of water, prior to the beginning of each run. An experimental run commenced by bringing the reactor containing pretreated catalyst to the desired temperature, maintaining helium flow for 1 hr at that temperature, then introducing cumene into the helium feed via a saturator in a constant temperature bath. Space velocities were varied by variation of the saturator temperature, which could be controlled to ±0.1°C. The reactor temperature was controlled, by means of heating tapes and insulation, to ±2°C. During the course of a run the relative amounts of cumene in reactor feed and effluent were determined periodically by chromatograph, and at the end of the designated run time the saturator was taken off stream and the catalyst cooled in flowing helium. The weight of the fouled catalyst was then determined and a representative portion was transferred to a chromatographic column for determination of effective diffusivity.

Effective diffusivities were determined by the chromatographic method detailed by Eberly (*9*), using SF$_6$ as the trace component in helium with a column temperature of 258 ± 2°C. The procedure requires determination of the shape-time characteristics of the SF$_6$ elution curves as a function of the interstitial velocity of the carrier gas. The height equivalent of a theoretical plate (HETP) can be determined from an elution curve using the relation recommended by Purnell (*11*):

$$\mathrm{HETP} = \frac{LW_e^2}{8t_m t_e}, \tag{1}$$

and the HETP is related to the interstitial velocity of the carrier gas, u, using the equation developed by Van Deemter, Zuiderweg and Klinkenberg (*12*):

$$\mathrm{HETP} = A + B/u + Cu. \tag{2}$$

In Eq. (2) the constant A is related to eddy diffusion in the column resulting from turbulent flow, B is related to longitudinal dispersion in the tracer pulse, and C – the quantity we are interested in – to mass transfer effects in the column. It is apparent that the last term in Eq. (2) will be predominant at high values of u, thus the constant C can be determined from the limiting slope of the HETP vs u curve at high velocities. Alternatively, all three constants can be determined by fitting Eq. (2) over the entire range of the data. Both methods were used in this work, with good agreement between the C values determined. From the value of the constant C, the effective diffusivity is determined according to the relationship determined by Eberly:

$$C = \left[\frac{(F_{\mathrm{I}} D_p)^2}{75 F_{\mathrm{II}}{}^2 D_{\mathrm{I}}} + \frac{F_{\mathrm{I}} K D_p}{2\pi^2 F_{\mathrm{II}} D_{\mathrm{eff}}}\right] (1 + K F_{\mathrm{I}}/F_{\mathrm{II}})^{-2} \tag{3}$$

where K, written to account for possible adsorption of tracer on the catalyst, is:

$$K = \frac{1}{\epsilon + \beta/F_{\mathrm{II}}}, \tag{3a}$$

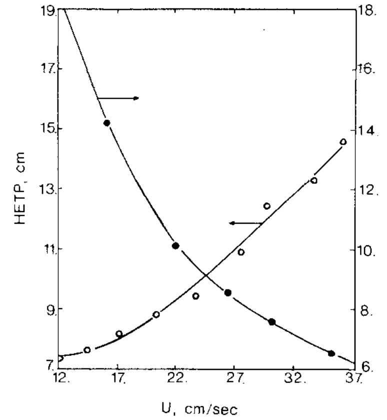

FIG. 1. Typical results for HETP vs u from chromatographic experiments, with corresponding nonadsorbable retention times.

Properties of columns	Catalyst	Glass
Coking conditions	260°C, 3 hr, 0.33SV	—
Coke content (%)	2.86	—
F_I	0.674	0.604
ϵ	0.316	0
D_p (cm)	0.284	0.284
L (cm)	76	76
T (°C)	258	258
D_I (cm²/sec)	1.08	1.08

Parameters determined: $U(t_m - t_0) = 14.2$ cm; $\beta = 0.126$; $K = 1.42$; $C = 0.46$; $D_{II} \times 10^3 = 1.7$ cm²/sec (D_{eff}).

and

$$\beta = \frac{(t_m - t_0)uF_I}{L}. \qquad (3b)$$

The nonadsorbable retention time, t_0, which is required to determine K is measured in a separate experiment under identical conditions using glass packing of the same size and shape as the catalyst studied such that the column properties (void volume, etc.) are the same as far as possible. A typical HETP curve with corresponding column properties and nonadsorbable retention time is shown in Fig. 1, where the solid line is the least squares fit of Eq. (2) to the experimental results.

RESULTS

Figure 2 gives some typical data on the activity decay of the mordenite on coking in terms of conversion relative to that on the fresh catalyst. Changes in activity are almost the same at 230 and 260°C for the 2 × 6 mm cylinders, while at 350°C there is a more rapid deactivation of the 12–16 mesh material than for the cylinders. These results are in good accord with those of Eberly and Kimberlin (*8*), particularly in view of the different temperatures in the present work. There is, however, either a chromatographic separation effect in the reactor or a substantial influence of side reactions (perhaps coke formation itself) on the fresh catalyst, since measured conversions (based on disappearance of cumene) at short times on stream are beyond equilibrium for the simple cracking of cumene to benzene and propylene. Hence we make use of the results of Fig. 2 mainly as a qualitative indication of the relative rates of deactivation under various conditions. For the heavily coked samples at lower temperatures though, conversions are well below equilibrium and we can make use of the data directly to estimate the rate of reaction. Two important points from Fig. 2 are: (i) the very rapid deactivation at 230 and 260°C, which will also be reflected in the coking data discussed below, and (ii) the effect of particle size observed at 350°C indicating strong diffusional limits on the reaction.

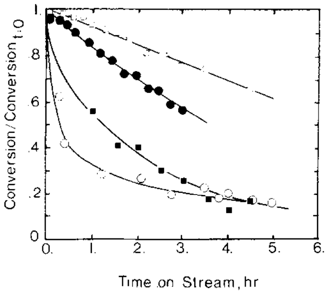

FIG. 2. Change of H-mordenite activity for cumene cracking at various temperatures, SV = 0.33 g/hr/g. (○) $T_p = 260$°C, $T_R = 230$°C; (■) $T_p = 260$°C, $T_R = 260$°C; (●) $T_p = 350$°C, $T_R = 350$°C, 2 × 6 mm; (□) $T_p = 350$°C, $T_R = 350$°C, 12/16 mesh.

Data for the amount of coke on catalyst vs time of utilization are given in Fig. 3 in

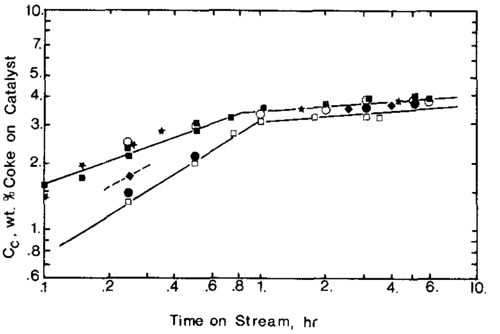

FIG. 3. Voorhies (*13*) correlation of coke deposition at various temperatures, SV = 0.33 g/hr/g. (○) $T_p = 260°C$, $T_R = 230°C$; (■) $T_p = 260°C$, $T_R = 260°C$; (⋆) $T_p = 350°C$, $T_R = 260°C$; (●) $T_p = 350°C$, $T_R = 350°C$, 2 × 6 mm; (◆) $T_p = 350°C$, $T_P = 300°C$; (□) $T_p = 350°C$, $T_R = 350°C$, 12/16 mesh.

the form of a Voorhies (*13*) correlation from experiments at 0.33 g/hr/g space velocity. As shown, there are two regions of the correlation in all cases: the left portion representing an initial rapid increase in coke content to a near-equilibrium level on the order of 3.5 wt%, and the right representing a subsequent very slow change in the amount of coke. The exponent *n* in the Voorhies correlation:

$$C_c = a\theta^n \tag{4}$$

for this series of experiments is given in Table 2. Coke deposition at the two lower temperatures is essentially the same and independent of the pretreatment conditions employed. At higher temperatures there appears to be a small dependence of coke deposition rate on particle size, with the larger particles actually coking to a higher level; however the Voorhies exponents are basically the same for the two sizes. A word of caution pertains to the values of *n* reported in Table 2. The larger values obtained for 350°C would indicate that the catalyst is more rapidly coked at higher temperatures. In fact, there is a much more rapid initial coke deposition at lower temperatures which implies the existence of yet a third portion of the correlation pertaining to times on stream of 1-2 min or less. In this region *n* values for the lower temperatures are greater than for 350°C.

TABLE 2

VOORHIES CORRELATION EXPONENTS

	n	
Run conditions	Initial	Final
230, 260°C, 0.33SV	0.40	0.10
350°C, 0.33SV	0.55	0.10

The effect of space velocity on coking rates is shown in Fig. 4 for the runs at 260°C. At 0.33 g/hr/g and above there is no influence of space velocity on the coke deposition. Similar results were obtained at the other temperatures and the subsequent discussion of transport properties is based on the results of experiments at 0.33 g/hr/g.

The change in intraparticle diffusivity, both in terms of time on stream and coke content, is shown in Fig. 5 for samples coked at 230, 260 and 350°C. The values shown are those for SF_6 tracer, measured at a temperature of 258 ± 2°C. The difference in values between the 12/16 mesh, 350°C samples and the 2 × 6 mm 230 and 260°C samples indicate some sensitivity of the chromatographic method to particle shape, particularly with regard to preparation of suitable columns to determine the

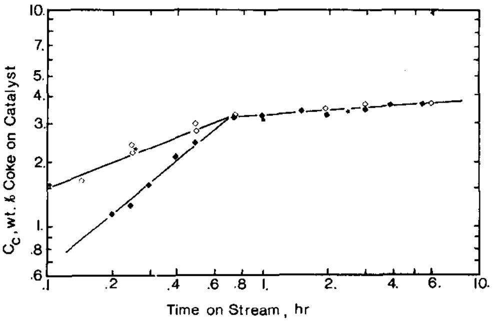

FIG. 4. Effect of space velocity on coke deposition at 260°C. (◆) SV = 0.20 g/hr/g; (◇) SV = 0.33 g/hr/g; (⋆) SV = 0.65 g/hr/g; $T_p = 260°C$; $T_R = 260°C$.

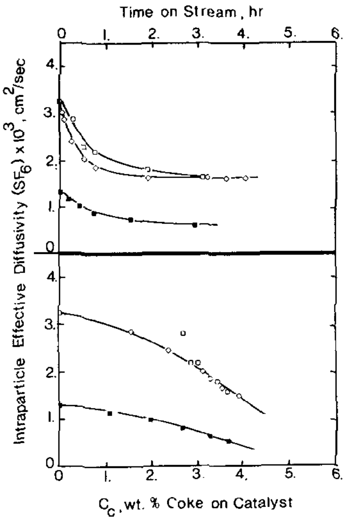

FIG. 5. Changes in effective diffusivity (SF_6, 258°C) of H-mordenite on coking in the temperature range from 230 to 350°C. (□) $T_R = 230°C$; (◇) $T_R = 260°C$; (■) $T_R = 350°C$ (12/16 mesh).

nonadsorable retention time for the irregularly shaped material. However, the important point is not so much the absolute value but the change in diffusivity with coke level, by a factor of about 2 in all cases, which is not linearly related to the coke content. Further, the variation in diffusivity relative to the value for the fresh catalyst, (D_{eff}/D^0_{eff}), is the same function of coke content for catalysts coked under all conditions of space velocity (≥ 0.33 g/hr/g), temperature and particle size employed in the experimentation. This result is shown in Fig. 6.

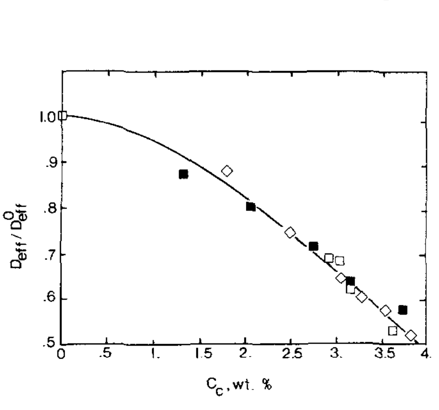

FIG. 6. Diffusivity relative to that of fresh catalyst. (□) $T_R = 230°C$; (◇) $T_R = 260°C$; (■) $T_R = 350°C$ (12/16 mesh).

DISCUSSION

In addition to the consequences of the diffusion–reaction interaction, the behavior of this system also appears to be influenced by the morphology of the coke deposition. Representative cross-sectional views of pellets coked for several hours at various temperatures reveal the existence of three distinct regions of coke deposition. A thin shell, very heavily coked, exists at the outer surface, while the center core is not coked at all. Between the center core and the surface shell the pellet is coked to an intermediate extent. The heavily coked outer shell is shown in cross section in Fig. 7a. As shown, the interparticle voids within the pellet are almost completely filled *at the surface*, but immediately below this surface layer an appreciable portion of the voids is not blocked. A view normal to the surface of the particle is given in Fig. 7b, where the coke appears as a glassy coating covering a large portion of the pellet exterior surface. The sample shown was on stream for 3 hr at 260°C; the average coke content of this batch of catalyst was 3.8 wt% and its diffusivity was 1.75×10^{-3} cm²/sec, 55% of the initial value of 3.2×10^{-3} cm²/sec.

The heavily coked outer shell shown in Fig. 7a is most apparent in samples coked at the lower temperatures. The similarity in activity decline and coke deposition observed at 230 and 260°C would seem reasonably interpreted as the result of the rapid initial formation of this outer layer; there is little visible difference between the deposits shown in Fig. 7 and corresponding view for samples reacted at 230°C. The change in activity subsequent to this initial shell formation is then strongly influenced by the rate of transport through the shell, which itself does not change much in structure after the initial period (~ 10 min) of catalyst utilization. At

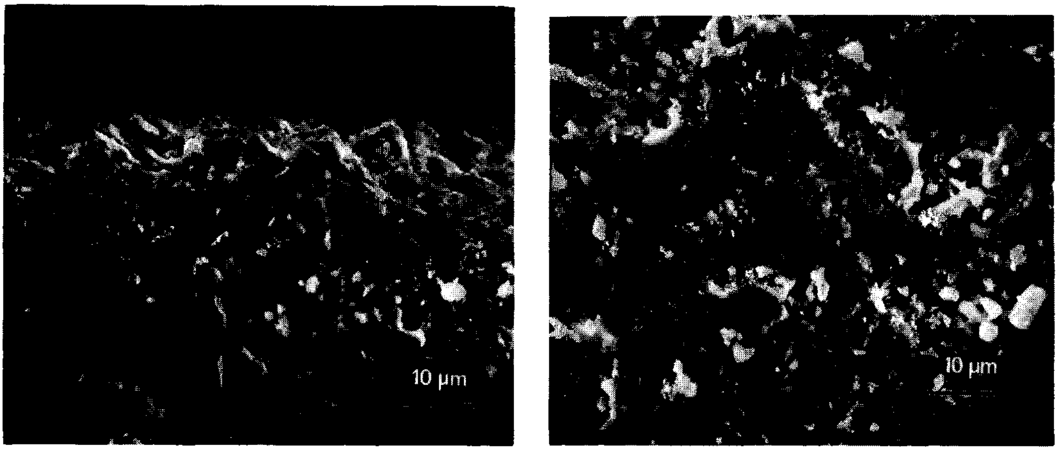

FIG. 7.(a) Cross section of heavily coked outer shell, $T_R = 260°C$, 3 hr. (b) View normal to the surface of the particle.

higher temperatures the initial adsorption and coke formation is not as rapid and the corresponding changes in activity and diffusivity are slower.

One of the most important implications of the change in effective diffusivity on coking is in the possible misestimation of the magnitude of diffusional limitation for a given reaction. Weisz and Hicks (*14*) have given a method whereby catalytic effectiveness can be determined from experimentally observable quantities. We determine the value of the modulus Φ_s:

$$\Phi_s = \frac{R_s^2}{D_{\text{eff}} C_0} (r_v), \tag{5}$$

Where R_s is the particle radius (spherical), r_v the rate of reaction per unit volume of catalyst, C_0 the concentration of reactant, and D_{eff} the effective diffusivity (corrected for the difference in molecular weights between cumene and SF_6), all experimentally observable. From the generalized plots of Weisz and Hicks, one may determine the effectiveness factor as a function of Φ_s. In addition, one may determine the value of the Thiele modulus, ψ, from:

$$\psi = \left(\frac{\Phi_s}{\eta}\right)^{1/2} \tag{6}$$

For the present experiments the thermicity parameter, $\beta = [(-\Delta H) C_0 D_{\text{eff}} / K_{\text{eff}} T_R]$, defined by Weisz and Hicks is very small (~ 0.01), so intrapellet thermal gradients are not important. An example of the influence of the variation in diffusivity on activity (effectiveness) estimates, based on isothermal theory, is given in Table 3 for the results at 260°C.

The numbers in Table 3 are not precise values, since an equivalent spherical radius has been used for the pellet dimension, and the rate and concentration values are average quantities for the integral bed with cumene conversion approximately 15%. However, they are sufficiently precise to establish the trend in relative values of effectiveness as they are influenced by the change in diffusivity. It is seen from the value of ψ in Table 3 that even the deactivated, heavily coked catalyst is in the "strong diffusion limitation" region with respect to the cumene reaction. The effectiveness factor is then inversely proportional to the Thiele modulus [defined as $(R_s/3)(k/D_{\text{eff}})^{1/2}$], and it is reasonable to assume that more active, less extensively coked catalysts would also be in this region of strong diffusion. The misestimation of effectiveness factor by using the

TABLE 3

INFLUENCE OF DIFFUSIVITY VARIATION ON EFFECTIVENESS ESTIMATES[a]

R_s (cm)	r_v (moles/sec-cm^3 cat)	D_{eff} (cm^2/sec)	C_0 (moles/cm^3)	Φ_s	η	ψ
1. Based on initial (fresh catalyst) diffusivity						
0.142	1.9×10^{-7}	3.2×10^{-3}	1.75×10^{-7}	6.9	0.67	3.25
2. Based on actual diffusivity						
0.142	1.9×10^{-7}	1.75×10^{-3}	1.75×10^{-7}	12.5	0.45	5.52

[a] Example: time on stream = 4 hr; coke content = 3.8%; SV = 0.33 g/hr/g; T_p = 260°C, T_R = 260°C.

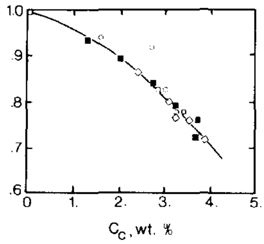

FIG. 8. Misestimation of effectiveness factor due to diffusivity variation.

incorrect diffusivity of fresh catalyst is then given simply by:

$$\eta/\eta^0 = (D_{\text{eff}}/D^0_{\text{eff}})^{1/2}. \tag{7}$$

The experimental results for (η/η^0) as a function of coke content are given in Fig. 8. As would be expected from the excellent correlation previously observed between diffusivity and coke content, essentially the same relationship between (η/η^0) and C_c exists for the samples coked at all temperatures investigated, and it is almost linear. For the more heavily coked samples the change in diffusivity alters the effectiveness factor estimate on the order of 25%, which we feel is a sufficiently large variation to warrant attention in the design of reactors involving coke deposition on very active catalysts.

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