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Radiotracer Experiments on Carbon Formation in Zeolites

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The origin of carbon deposits in zeolite catalysts was traced with radioactively labeled mixtures of hexane and aromatics (100–500 psia H_2). Over mordenite and Y catalysts of varying aluminum content it was shown that the participation of aromatics in coke formation was equal to or exceeded that of the paraffin. Such participation decreased with increasing temperature or, in the case of mordenite, with increasing SiO_2/Al_2O_3 ratio, but was little affected by changes in hydrogen pressure. It was concluded that the alkylation of aromatics is the initial step in coke formation in the present experiments and that hydrogen transfer, an important reaction in the subsequent transformations of carbon deposit, need not be invoked to explain the original deposition.

INTRODUCTION

Studies of coke formation and aging in hydrocarbon processing are numerous and are central to the practical application of solid acid catalysts such as silica–alumina and zeolites (*1*). Excluding from consideration any physically sorbed residues, these carbonaceous deposits tend to be pseudographitic or aromatic in nature, their H/C ratios depending on the specific conditions of their formation (*2–7*). The residues tend also to be rather refractory, radiotracer experiments indicating little carbon exchange between a coke deposit and a reacting paraffin hydrocarbon (*6*). Venuto and Hamilton (*5*) proposed that zeolite catalyst aging was an example of "reverse molecular-size selectivity." These authors established the polyalkyl-aromatic nature of the coke residue from reaction of benzene and ethylene and concluded that catalyst deactivation was associated with the occlusion of such large molecules within the catalyst (X-type zeolite) pore. Most recently, evidence has been presented to suggest that ease of coke formation is an intrinsic property of zeolite pore structure, the spatial restrictions in small-pore zeolites often severely inhibiting formation of coke and of its precursors (*8*).

The chemical origin of these coke deposits has occasioned an equally great interest. In one of the earliest studies (*9*) a direct relationship between coke deposited and aromatic, especially polynuclear aromatic, content of the feed was observed over silica–alumina catalysts. Subsequent studies confirmed this observation and showed a proportionality between coke formation and the basicity of a variety of aromatic compounds (*10–12*).

Compounds other than aromatics can contribute to coke formation as well, as shown by studies with paraffins and olefins (*13–17*). Using radioactively labeled C_7 and C_8 olefins and paraffins as feeds, it was shown that all carbon atoms participated equally in coke formation (*16*). Experiments with *n*-decane-2-^{14}C, however, showed that such equal participation was

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not a characteristic general to all temperatures and to paraffins of all molecular weights (*17*).

The above discussion has treated the nature of coke deposits and the relative ease of coke formation from various hydrocarbons. Underlying coke deposition is the fundamental concept of hydrogen transfer (*18–22*). The suggestion that hydrogen transfer was responsible for the formation of paraffins, aromatics, *and* a hydrogen-deficient carbonaceous deposit in the conversion of olefins over silica–alumina was originally presented by Thomas (*18, 19*). Radiotracer experiments with mixtures of 1-butene and decalin provided further evidence for the relationship between hydrogen transfer and coke formation over silica–alumina catalysts (*20*). The unusually high hydrogen transfer activity (relative to cracking) characteristic of zeolite catalysts, however, revealed that, although hydrogen transfer is an important reaction in coke formation, it cannot be the dominant consideration. Zeolites, with their higher hydrogen transfer activity, make *less* coke and dry gas than do silica–aluminas (*21, 22*).

In the following experiments, radiotracers have been applied to an analysis of the origin of the carbonaceous deposits on zeolite catalysts. Mixtures of paraffin and aromatic were used as feeds in order to simultaneously afford the potential reactions of cracking, olefin polymerization, and alkylation of aromatics (*8*). Hydrogen pressure was applied to retard coke deposition rates and to thereby provide an opportunity for selectivity in that deposition. The presence of hydrogen was also intended to reduce effects of changing feed mixture.

EXPERIMENTAL

Catalytic Runs

Experiments were conducted in a downflow, stainless steel reactor, 13.2 cm long, 1.5 cm in diameter, with a 0.3-cm thermowell in the center, all preceded by a 20-cm preheater spiral. Hydrocarbon was metered to the reactor with a Milton-Roy piston pump, and liquid products were taken off under pressure and weathered, together with the total gas effluent, through a liquid nitrogen trap. Liquids were analyzed on a 50-m polyphenylether (OS124, Applied Science Laboratories) × 0.025-cm capillary column, programmed from 25 to 160°C; the product in the liquid nitrogen trap on a 3-m Poropak Q column. Hydrogen and methane were passed through a wet test meter and were analyzed by mass spectroscopy. Material balances were 97% or better.

Reaction conditions are given, together with conversion data, in the appropriate tables. Conditions were varied about a "base case" of 200 psig, $H_2/HC = 1.4$, 360°C, WHSV = 2.0, 3 h on stream. The base case feed was a 1:1 molar mixture of benzene and hexane, one component of which was labeled with ^{14}C. Overall hexane conversion was 10–20% in these experiments. At the conclusion of each run the catalyst was cooled under flowing hydrogen to remove any physically sorbed hydrocarbon.

Catalysts for these experiments were Y (Strem) and mordenite (Norton) zeolites of varying SiO_2/Al_2O_3 ratio, as follows: Y: $SiO_2/Al_2O_3 = 5.3$, 8.5, and 13.2; and mordenite: $SiO_2/Al_2O_3 = 18$, 40, and 108. The last two Y samples were dealuminized with EDTA according to techniques developed by G. T. Kerr (*23*). All Y samples were exhaustively NH_4-exchanged (Na/Al below 0.05). The intermediate mordenite was kindly supplied by D. H. Olson, the others being from Norton. Crystallinity of all zeolite samples exceeded 75% by X-ray diffraction. All catalysts were sized to 60/80 mesh and were calcined to 500°C overnight prior to testing, X-ray diffraction establishing their crystal integrity.

Tracer Analysis

Radiotracers were obtained from CalBio Nuclear and from Amersham-Searle. Hexane, labeled in the 1-position, had been prepared by hydrogenation of 1-hexanoic acid and was percolated over activated alumina prior to use.

Product (and feed) analysis for ^{14}C was performed by combustion to CO_2, trapping, and counting (Packard 3375 liquid scintillation counter). Samples were burned in a 45-cm quartz tube (2.5 cm inner diameter) over copper oxide (held in place by two Pt gauze screens) at ~900°C in an oxygen stream (oxygen:hydrocarbon $\geq 7:1$). Liqquids were fed into the oxygen stream by a syringe pump; gases, by water displacement. Coked catalysts was placed in a separately heated prereactor chamber. In addition to total liquid product, liquid fractions, separated by distillation into "hexanes" (35–71°C), "benzene" (72–82°C), and alkyl-aromatics (83°C$^+$), were burned for a more detailed analysis.

Following the combustion tube, water was removed in an acetone–dry ice trap; CO_2 was removed by an amine sorbent, Carbosorb II (Packard Instruments). Periodic gas–liquid chromatographic analysis of the product gas showed no detectable CO. Water plus CO_2 balances generally exceeded 97%.

For counting, 1 ml of the Carbosorb II–CO_2 solution was added to 14 ml of Instafluor scintillation solution (Packard). The observed counts per minute (cpm) were corrected to disintegrations per minute (dpm), using the channels ratio method (*24*, *25*), by comparison with the counts per minute for a sample of known radioactivity. Counting efficiencies were in the range 79–83%.

Total radioactivity balances were determined for several runs and exceeded about 95%. Disintegrations per minute per gram of carbon were reproducible to ±5%, leading to an uncertainty in the origin of any given product of less than ~3.5%. Radioactive analysis of both benzene and hexane product fractions showed no carbon scrambling between the two feed components.

RESULTS

Data were initially obtained with hexane–benzene feeds (and subsequently with a mixture of hexane and 1,3,5-trimethylbenzene) and were designed to separate the influences of feed composition, reaction conditions, and SiO_2/Al_2O_3 ratio on coke formation.

The results are presented in Table 1 for the mordenite samples in order of decreasing SiO_2/Al_2O_3 ratio, each experiment being selected to examine a different variable. The results showed the following, with particular reference to coke.

(a) At a high SiO_2/Al_2O_3 ratio, paraffin and aromatics contributed almost equally to coke formation (experiments 1 and 2).

(b) Such equal participation was unaffected by a substantial reduction in H_2 partial pressure (although the total coke yield increased).

(c) The participation of aromatics in coke formation increased as their content in the feed increased, but not disproportionately. At a benzene/hexane mole ratio of 2, 62% of the carbon in the coke came from benzene, essentially the same as the aromatic carbon content of the feed (67%).

(d) As the SiO_2/Al_2O_3 ratio of the mordenite catalyst decreased, both the participation of the aromatics and the coke yield increased (experiments 1, 5, and 6).

(e) An increase in temperature with a low SiO_2/Al_2O_3 mordenite catalyst sharply reduced the contribution of aromatics to coke formation and somewhat reduced coke yield.

(f) Only about 5% of the light gas products came from benzene, a fraction which could well be attributed to continuing transformations in a deposited coke.

TABLE 1

Product Origins over Mordenite (Benzene:*n*-Hexane Feed, 360°C, WHSV 2)

	1	2	3	4	5	6	7[a]
Runs conditions							
Benzene/hexane ratio	1	1	1	2	1	1	1
Label	NC6	A6	NC6	NC6	NC6	NC6	A6
SiO_2/Al_2O_3	108	108	108	108	40	18	18
H_2, psia	125	125	30	120	120	125	125
HC, psia	90	90	90	95	95	90	90
Derived from benzene							
Coke, %	47	48	51	62	54	63	39
Light gas, %	5	6	5	1	4	7	8
Coke yield (g/100 g of conversion)	6.6	6.8	8.8	6.8	11.8	16.9	10.2

[a] 454°C.

Mordenite is a pseudo-two-dimensional, 12-ring zeolite of moderately high SiO_2/Al_2O_3 ratio. The origin of coke in a 12-ring zeolite of lower SiO_2/Al_2O_3, zeolite Y, is shown by the results in Table 2. For the Y sample, the following results were found.

(a) Aromatics were the major contributor to coke formation, accounting for almost 80% of the carbon deposited at low temperature (360°C). Their contribution was rather insensitive to increasing SiO_2/Al_2O_3 (experiments 8–11), to varying hydrogen partial pressure, and to longer contact time. They increased only slightly with increasing benzene content in the feed.

(b) About 15–20% of the light gas came from benzene, a significantly higher fraction than was found with mordenite.

(c) Coke yield and participation of

TABLE 2

Product Origins over Y (Benzene:*n*-Hexane Feed, 360°C, WHSV 2.3, Unless Noted)

	8	9	10	11	12	13	14[a]	15	16[b]	17[b]	18[c]
Run conditions											
Benzene/hexane	1	1	1	1	1	1	1	2	1	1	1
Label	NC6	A6	NC6	NC6	NC6	NC6	A6	NC6	NC6	NC6	NC6
SiO_2/Al_2O_3	5.3	5.3	8.5	13.2	5.3	5.3	5.3	5.3	5.3	5.3	5.3
H_2, psia	125	120	120	130	30	495	155	120	120	155	125
HC, psia	90	95	95	85	95	75	60	95	95	60	90
Derived from benzene											
Coke, %	78	79	78	76	75	79	72	83	60	59	79[d]
Light gas, %	22	25	19	11	13	12	14	13	0	8	16[d]
Coke yield (g/100 g of conversion)	37	36	38	33	46	36	35	43	30	20	9[e]

[a] WHSV 1.3.

[b] 454°C.

[c] 1,3,5-Trimethylbenzene:hexane.

[d] On a molar basis.

[e] Conversion includes trimethylbenzene disproportionation.

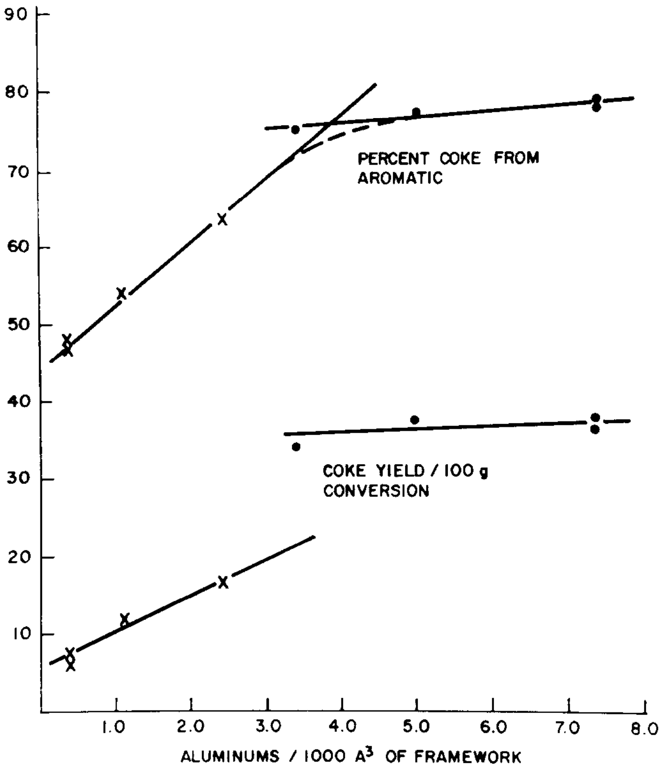

FIG. 1. Aromatic participation in coke formation and coke yield/100 g of conversion for Y (●) and for mordenite (X) catalysts of varying aluminum density (360°C).

aromatics in carbon deposition decreased sharply when the temperature was increased. At the higher temperature there was little contribution from benzene to light gas production.

(d) The origin of coke and of light gas was insensitive to the structure or reactivity of the aromatic, as shown by the experiment with 1, 3, 5-trimethylbenzene.

DISCUSSION

Paraffin cracking is obviously not the only reaction which occurs when a mixture of hydrocarbons is passed over a zeolite catalyst. The olefinic fragments of cracking undergo polymerization, aromatization, and coking reactions; they may alkylate aromatics present in the reaction mixture. Aromatics can disproportionate or undergo transalkylation reactions. Most fundamental to the practical use of a zeolite catalyst, however, is its coking tendency, and related thereto, the origin of that coke. The data in Tables 1 and 2 have permitted distinction to be drawn between origin and yield of these carbon deposits.

As discussed earlier (*8*), coking tendencies are intrinsically related to zeolite pore structure, being particularly strong in large-pore structures such as Y and mordenite. Superimposed on this inherent proclivity of large-pore structures to coking can be a substantial influence of aluminum content. Plotted in Fig. 1 are aromatic participation and coke yield as a function of aluminum *density* in the two zeolite structures examined. In a Y zeolite there are about 13 Si or Al tetrahedra per 1000 Å^3; in a mordenite, 17. The framework structure in a Y occupies 50% of the unit cell volume, as compared with 70% in a mordenite (*26*). A framework aluminum density can then be calculated which would offer an approximate measure of the zeolite surface composition encountered by reactant molecules as follows:

Zeolite	SiO_2/Al_2O_3	Al/1000 Å^3 of framework
Y	5.3	7.4
	8.5	5.0
	13.2	3.4
Mordenite	18	2.4
	40	1.1
	108	0.4

[The tendency of a Y zeolite to loose framework aluminum on calcination, to form "ultrastable Y," complicates the analysis (*30*). Its effect would be to reduce the difference between the three Y samples. The mordenite would be unaffected. All three Y zeolites showed lattice contractions after calcination and NH_3 treatment and should be regarded as ultrastable samples.]

As one would expect, coke yields generally increased with increasing aluminum content. Significant in the yield plot, however, is the discontinuity between Y and mordenite trends, coke formation in Y being intrinsically more facile. This distinction, reported in earlier experiments (*8*), is attributed to the large cavities which result from intersection of the three-dimensional pore channels present in Y but absent in mordenite.

In the chemical *origin* of those carbon deposits, however, a limiting contribution of aromatics is observed with increasing aluminum content in the six samples investigated, and the dashed line in Fig. 1 postulates that this contribution may be independent of zeolite structure. (Mordenites cannot be made with an aluminum content above 4 per 1000 Å^3 of framework, i.e., SiO_2/Al_2O_3 below 10, so the postulate cannot be directly tested.) Such a trend is attributed to selective adsorption of benzene (as opposed to hexane) at the low temperature of these runs (360°C), a preference which increases as the aluminum density in the framework increases. Several authors have reported selective adsorption of aromatics in noncatalytic experiments (*26–28*), a selectivity which decreases with increasing SiO_2/Al_2O_3 ratio of a zeolite (*29*). Once the surface is covered with aromatics a limiting behavior would be expected which would be little affected even by doubling the aromatic content of the feed (experiment 15). The sharp decrease in the contribution of aromatics to coke formation with increased temperature is in good agreement with this explanation.

In addition to its substantial, even dominant role in coking, a parallel participation of aromatics in light gas formation is evident in Tables 1 and 2. It is suggested that such a participation evidences the continuing transformations of intracrystalline "coke" under these reaction conditions, rather than any new reaction path for the conversion of aromatics. The parallel between coke and light gas origins supports such a suggestion.

Finally it is proposed that, in these reactions of paraffin–aromatics mixtures over large-pore zeolites, the initiating reaction in coke formation is alkylation of aromatics and that coke results from the continuing transformation of these alkylated intermediates. Evidence for this proposal is: (a) The equal or preferential incorporation of aromatics into coke, the experiment with trimethylbenzene indicating that direct reactions such as disproportionation are not strong coke producers; (b) the proportionality between aromatic content of the feed and that of the carbon deposits in the reactions over mordenite; and (c) coke yield *but not origin* was influenced by major changes in hydrogen partial pressure.

CONCLUSIONS

Radiotracer experiments on the conversion of benzene–hexane mixtures over mordenite and over Y zeolites showed a substantial aromatic contribution to coke formation which increased with increasing aromatic content of the feed and with decreasing temperature, and which approached a limiting value as framework aluminum density increased. That contribution was insensitive, however, to hydrogen partial pressure. An aromatic contribution to light gas make was observed, probably occurring via a coke intermediate.

It was proposed that the initial reaction in coke formation in these experiments was the alkylation of aromatics by the olefinic fragments of paraffin cracking. Hydrogen transfer is assigned a major role in the continuing transformation of a coke deposit, but need not be invoked in the initial coke formation step.

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