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Radiotracer Experiments on Carbon Formation in Zeolites. II

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Carbon deposition in a 10-ring zeolite was traced with radioactively labeled mixtures of hexane and aromatics and was compared with earlier results on 12-ring structures. Although coke yields differed by 1 to 2 orders of magnitude between the two structural classes, it was shown that the origin of the carbon deposits in both was strikingly similar, involving nearly equal participation of both paraffin and aromatic. The data supported the assertion that coke results from the transformation and reaction of alkylaromatics, those transformations being sterically inhibited within the restrictive dimensions of a 10-ring pore.

INTRODUCTION

Using the conversion of C_6 paraffin isomers, benzene, and toluene as a probe to examine a range of common zeolite catalysts, it was shown that systematic relations exist between sorptive properties, pore structures, and selectivities for hydrocarbon reactions, *including coke formation* (*1*, *2*). Those catalysts exhibiting shape selective activity also showed low coking and aging rates, and it was postulated that coking reactions may be spatially demanding and that intracrystalline coking (aging) rates may be intrinsic properties of zeolite pore structure.

Radiotracer studies with large-pore, 12-ring zeolites (mordenite and Y) using the hydrocarbon mixtures cited above showed that both aromatics and paraffins participate significantly in carbon deposition (*3*). At lower temperatures or with catalysts of higher framework aluminum content, aromatics dominated, probably due to selective adsorption effects, but when these effects were eliminated, a nearly equal paraffin–aromatic participation in coke formation was found, suggesting aromatics alkylation as the key step in the eventual formation of coke.

Publication of the structure of a 10-ring, shape-selective zeolite whose pores admit aromatics (*4*, *5*, *7*), presented an opportunity to test these suggestions. In the following pages, the origin of coke deposits in this zeolite, designated ZSM-5, is examined by radiotracer techniques and is compared with the results reported earlier on mordenite and on Y.

EXPERIMENTAL

Details of the catalytic experiments and of the radiotracer analyses were described earlier (*3*). Reaction conditions were varied about a "base case" of 360°C, 200 psig, $H_2/HC = 1.4$, WHSV 6, 3 hr on stream. Conversion of *n*-hexane was held constant (so far as possible) and was in the range of 75–90%.

Radiotracers were obtained from Cal Bio Nuclear, and their distribution in the products was determined by combustion

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to CO_2 (*3*). Product liquids were fractionally distilled and showed no carbon scrambling between benzene and hexane feed components.

Two samples of zeolite were examined, both having crystal diameters of about 0.3 μm, and were designated ZSM-5(72) and ZSM-5(25), the numbers in parenthesis representing SiO_2/Al_2O_3 mole ratios. Each sample was calcined in nitrogen to 500°C, treated with NH_3, and exhaustively exchanged with aqueous $(NH_4)_2SO_4$ to remove sodium. Zeolite samples were sized to 60/80 mesh and were calcined to 500°C overnight prior to use. X-Ray diffraction showed retention of crystal integrity during exchange and testing.

RESULTS

Data were obtained with benzene:*n*-hexane or 1,2,4-trimethylbenzene:hexane mixtures and are summarized in Table 1, with the following observations:

(a) With the high SiO_2/Al_2O_3 sample, benzene and hexane participated equally in coke formation, a result which could not be attributed to residual, sorbed hydrocarbons. Forty-eight percent of the coke came from benzene with a 1:1 feed, 59% (vs 67% theoretical) with a 2:1 mixture.

(b) The proportional contribution of aromatic and paraffin to carbon deposition is unaffected by H_2 partial pressure, by temperature, or by aromatic reactivity. Aromatics contributed 47–49% of the coke with benzene:hexane mixtures, 47% with the 1,2,4-trimethylbenzene:hexane feed.

(c) When the framework aluminum content of the ZSM-5 catalyst was increased, a *decrease* in the aromatic contribution to coke was found (a distinct contrast from the observations with 12-ring zeolites).

(d) In no case did aromatic contribute significantly to light gas formation.

DISCUSSION AND CONCLUSION

The results reported earlier for the large-pore mordenite structure (*3*) showed a progressive increase in coke yield and in aromatics contribution to coke with increasing framework aluminum content, a trend attributed to preferential adsorption of aromatic at low temperatures (360°C). ZSM-5 shares some structural and compositional features with mordenite,

TABLE 1

Product Origin[a]

	1	2	3[b]	4	5	6[c]	7[d]	8[e]
Run condition								
Aromatic/hexane ratio	1	1	1	2	1	1	1	1
Label	NC6	A6	A6	NC6	A6	A6	NC6	NC6
WHSV	6	6	6	7	7	21	7	19
H_2 (psia)	125	120	125	115	30	120	125	145
HC (psia)	90	95	90	100	100	95	90	70
Derived from aromatic								
Coke (%)	49	47	51	59	48	54	47	30
Light gas (%)	3	2	1	0	0	3	2	1
Coke yield (g/100 g of conversion)	0.23	0.24	0.15	0.35	0.27	0.16	0.51	0.22

[a] Benzene:*n*-hexane feed, 360°C, $SiO_2/Al_2O_3 = 72$, unless noted.

[b] Catalyst treated 3 hr, 300°C, in flowing N_2 to remove any sorbed hydrocarbons.

[c] 454°C.

[d] 1,2,4-Trimethylbenzene:*n*-hexane; coke origin on molar basis.

[e] $SiO_2/Al_2O_3 = 25$.

despite its differing pore size and its characterizing X-ray diffraction pattern (*5*). Both structures are based on 5-ring building blocks and contain the T_8O_{16} units described by Breck (*6*), and both have similar void fractions, 28% for mordenite and 29% for ZSM-5. Both structures can exist in a broad range of high SiO_2/Al_2O_3 ratios, mordenite by dealuminization and ZSM-5 by direct synthesis. Mordenite contains about 17 tetrahedra per 1000 Å^3; ZSM-5, 18.

Using this information, and the data reported earlier for mordenite (*3*), coke origins and yields can be compared between ZSM-5 and mordenite samples of the same framework aluminum content, as follows:

Zeolite	Al/1000 Å^3 of framework	Coke from aromatic (%)	Coke yield (g/100 g conversion)
ZSM-5	0.7	48	0.23
	1.9	30	0.22
Mordenite	0.7	49	8.5
	1.9	59	10.8

Almost *two orders of magnitude* distinguish coke yields on ZSM-5 from those on mordenite catalysts, despite the fact that the origins of the carbon deposits at low framework Al density are virtually identical. Furthermore, as the ZSM-5 framework becomes more aluminum rich, *paraffin* (rather than aromatic) contributes increasingly to the coke produced.

Since composition has been normalized in the above comparison, the significant difference between these mordenite and ZSM-5 samples must lie in the size of the pore, ZSM-5 being a 10-ring, mordenite, a 12-ring structure. Differences in coke yields between the two structures are readily understood in terms of spatial constraints, the alkylaromatics, once formed, being prevented from reacting further to produce coke (by cyclization, hydrogen transfer, repeated alkylation, etc.) in the smaller ZSM-5 pore.

Regarding the variation in origins with framework Al content, in a 10-ring structure, whose pores cannot accommodate a concentration (preferential adsorption) of aromatics, it is proposed that an increase in acid site density leads directly to an increase in paraffin cracking fragments (carbonium ions) within the pore system and thus to the greater paraffin participation in coke. The key observation, however, is that the gross differences in coke yields between 10- and 12-ring zeolites are not the result of differing basic origins of that coke, but that they must arise from structural constraints on the reactions of the same intermediates in the formation of that coke.

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REFERENCES

1. Rollmann, L. D., *J. Catal.* **47**, 113 (1977).
2. Walsh, D. E., and Rollmann, L. D., *J. Catal.* **56**, (1979).
3. Walsh, D. E., and Rollmann, L. D., *J. Catal.* **49**, 369 (1977).
4. Argauer, R. J., and Landolt, G. R., U. S. Patent 3,702,886 (1972).
5. Kokotailo, G. T., Lawton, S. L., Olson, D. H., and Meier, W. M., *Nature* (*London*) **272**, 437 (1978).
6. Breck, D. W., "Zeolite Molecular Sieves," p. 46. John Wiley, New York, 1974.
7. Chen, N. Y., and Garwood, W. E., *J. Catal.* **52**, 453 (1978).