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Shape Selectivity and Carbon Formation in Zeolites

The systematics of shape selectivity in common acid zeolite catalysts was recently examined (*1*), and the overwhelming importance of zeolite pore structure in determining paraffin isomerization and cracking selectivities and aromatics alkylation propensities was demonstrated. More important, it was suggested that coke formation is a shape-selective reaction and that coking tendency (and aging rate) is an intrinsic property of zeolite pore structure.

These common zeolites fall into two groups, the large-pore structures such as Y, L, and mordenite, and the shape-selective ferrierite and erionite zeolites. The former group admits both aromatics and paraffins, while only paraffin (and, in fact, only normal paraffin) can enter the pore system of the latter. Radiotracer experiments with mordenite and with Y have shown that aromatics can contribute substantially to coke formation in zeolite catalysts, a contribution which increases with increasing framework aluminum content (decreasing SiO_2/Al_2O_3) and with decreasing temperature (*2*). Thus a key experiment remained to test the suggested correlation between coke formation and pore structure. Namely, a shape-selective zeolite was required which would admit aromatics as well as paraffins.

The purpose of this note is to present coking data for a broad spectrum of zeolite catalysts, many of which are relatively new, do not occur in nature, and are of unknown structure. Included in this survey are the zeolites, Y, L, mordenite, ferrierite, and a large number of ZSM-series samples beginning with ZSM-4, ZSM-5, etc., all of which are described by Breck (*3*) or in the recent patent literature.

Special attention was given to ensure that the results of this survey were not distorted by changes in composition (SiO_2/Al_2O_3 ratio) or in crystal size. Thus several samples of the same zeolite were often included which differed in both respects. An overlap was thereby established between the "large-pore" and the "shape-selective" groups (defined below) as follows:

Group	SiO_2/Al_2O_3
Large pore	5.3–108
Shape selective	7.6–220

The test reaction employed a five-component feed, comprising equal weights of *n*-hexane (NC6), 3-methylpentane (3MP), 2,3-dimethylbutane, benzene (A6), and toluene (A7) and was conducted at 427°C, 200 psig, and 3:1 H_2:hydrocarbon. Space velocity was varied (WHSV = 3–15) in order to permit measurement of the relative rates of conversion of the individual hexane isomers and in order to maintain a similar overall conversion level across the different zeolites. All catalysts were 60/80 mesh; all were calcined at 500°C from the ammonium form.

The observed coke yield (per 100 g of paraffin converted) is plotted in Fig. 1 against the ratio of first-order rate constants, k_{NC6}/k_{3MP}, for disappearance of

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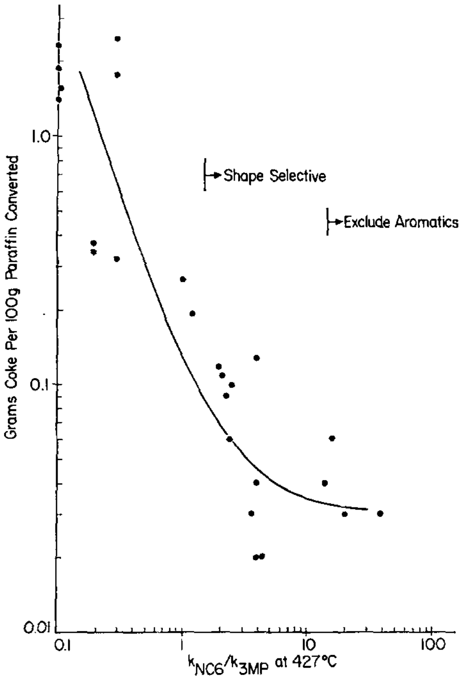

FIG. 1. Coke yield vs shape selectivity of paraffin conversion for acid zeolite catalysts.

the respective paraffin isomers. As is evident from the plot, an extreme flexibility is possible in the choice of zeolite catalysts. More important to the question of carbon formation, *order of magnitude* changes in coke yields accompany the transition from large-pore to shape-selective ($k_{NC6}/k_{3MP} > 1$) zeolites.

These changes in coke yield cannot be attributed to exclusion of aromatics from the latter's intracrystalline pore system since, as noted in Fig. 1, numerous shape-selective samples sorbed and converted aromatics. The efficiency of aromatics alkylation (by cracked paraffin fragments) in the latter samples averaged 9%, as compared with 10% in the large-pore zeolites, an experimentally insignificant difference. Those shape-selective zeolites open to aromatics show a preferential conversion of benzene rather than toluene ($k_{A6}/k_{A7} \sim 1.7$, as compared with ~ 0.3 for the large-pore samples), a preference attributed to diffusion restrictions on the respective alkylated aromatic product.

In summary, a correlation has been demonstrated between coking tendency and shape selectivity for a large number of zeolite samples of differing structure, composition, and crystal size. While composition and crystal size can certainly influence coke formation, the present survey suggests that these are secondary effects. The survey supports the postulate that intracrystalline coking is a shape-selective reaction directly controlled by zeolite pore structure (*1*).

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