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Carbon-14 Tracer Studies of the Secondary Reactions in the Cracking of Hexadecane over Zeolite Catalysts

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Results from cracking runs over zeolites using propylene tracer showed that incorporation of radioactivity into other products was not as large as when amorphous silica-alumina was used. (Bordley, J. L., Jr., Doctoral Thesis, Johns Hopkins University, Baltimore, 1972). The values for α, the ratio of the radioactivity of the products per unit volume to the radioactivity of the tracer per unit volume, were only about one-tenth of those for the corresponding products obtained when a standard amorphous silica–alumina (Davison #980) catalyst was used. Results from the runs using toluene tracer showed that almost all the radioactivity remained in the toluene on both types of catalysts. Values of α for toluene were as large or larger on the zeolite catalyst than on the standard silica–alumina catalyst.

INTRODUCTION

Zeolites have been used in commercial catalytic cracking for about a decade. Reported activities of these zeolites as compared to amorphous silica–alumina have varied widely. Plank and Rosinski have reported that the increase in activity is on the order of 10^3 (*2*) and that for rare earth faujasite the activity for cracking gas oil is over 100 times greater (*3*). Weisz and Miale reported that for cracking *n*-hexane the reactivity is as much as 10^4 times greater than over conventional silica–alumina (*4*, *5*).

In light of these reports, the current work was divided into two parts: (i) a preliminary study of several zeolite catalysts (CREX, CREY, USY)[3] to determine their cracking characteristics compared to the Davison #980 silica–alumina used previously in this laboratory and (ii) an extension to these zeolites of the work of van Hook (*7*), Hightower (*8*), and Bartley (*9*) who used carbon-14 tracers to examine the secondary reactions occurring during the cracking of hexadecane over the silica–alumina catalyst.

Two carbon-14 tracers were chosen to help study the secondary reactions. Propylene was used because of its high reactivity, particularly in forming aromatics. Toluene was chosen because of its large size relative to the pore size.

PRELIMINARY WORK: ISOPENTANE CRACKING

The purpose of the preliminary work was to compare the isopentane cracking over zeolite and silica–alumina catalysts. The regeneration procedures and cracking activities were studied by using a single sample of each catalyst, in turn, for a series of cracking reactions (Fig. 1). The pretreat-

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[3] CREX is a 13X zeolite exchanged with rare earth cations. CREY is the rare earth-exchanged 13Y zeolite. USY is the ultrastable Y zeolite described by McDaniel and Maher (*6*).

ment procedures were studied by cracking reactions on fresh samples of one of the catalysts, CREX (Fig. 2).

Experimental

In all the preliminary runs, 1 g of the zeolite was mixed with about 22 g of porous glass (100 mesh). The standard pretreatment procedure involved evacuating the sample with a mechanical pump while slowly warming it to the reaction temperature, 440°C. The reactor was then warmed further to the regeneration temperature while water-saturated air flowed at about 100 cm^3/min. The standard time for this oxidation step was 8 hr. Then the reactor was cooled to the reaction temperature, and helium was swept through the reactor at about 50 cm^3/min.

The cracking run consisted of passing a 2.7:1 helium:isopentane gas mixture over the catalyst for 30 min. A sample of the product stream was captured in a sampling apparatus at the end of 3 min and analyzed with an Aerograph Model A-90-P gas chromatograph. The same procedure was followed at the end of 10 and 20 min.

The regeneration procedure was then started. The sample was oxidized, usually with the wet air for 8 hr, at 520°C. The reactor was then cooled to the reaction temperature for the next run while being swept with helium. In the later runs, when a fresh sample of CREX was used each time, there was no regeneration step. During these same runs the temperature, oxidizing gas, and/or time of oxidation were varied during pretreatment.

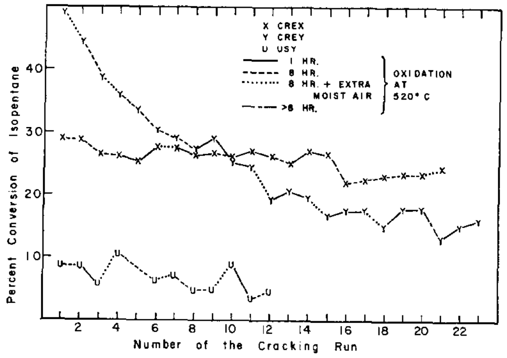

FIG. 1. Activity of CREX, CREY, and USY catalysts for the cracking of isopentane as a function of regeneration procedure.

Results and Discussion

From 12 to 23 runs were made with each catalyst sample of CREX, CREY, and USY. The results are plotted in Fig. 1 as percentage of conversion of isopentane at the 10-min sampling vs the number of the cracking run. Different symbols represent the exact conditions of regeneration between each run.

The CREX catalyst shows remarkable stability over a series of 20 runs and regenerations. The activity, expressed as percentage of conversion of isopentane to other products, the bulk of which are of carbon number C_5 or less, varies only from the initial 29 to 22%. The only regeneration procedure which made any noticeable change (decrease) in rate was the one before the 16th run when the oxidation was carried out for 24 hr. However after several shorter regeneration periods the activity increased again to about the average level.

Unlike the CREX, the CREY activity dropped considerably and only later leveled off. Thus, although the initial activity was much higher, 49%, than that of CREX, the final, "leveled off" activity was lower, about 18%. The 1-hr regenerations caused the least drops in activity, and in some cases the activity increased. As with the CREX, a particularly long regeneration of 39 hr caused a noticeable drop in activity.

The activity of the USY catalyst was relatively low (5–10% conversion) compared to the CREX and CREY samples. However it was fairly stable and changed its activity little during 12 runs. It may be noted from Fig. 1 that the moist air treatment during regeneration enhanced the activity of the USY catalyst whereas it seemed to cause a loss in activity for both the CREY and the CREX samples.

In the main work, to follow, each catalyst would be used only twice. From the above results it was assumed that one regeneration of about 8 hr at 500°C made no great change in the cracking abilities of the catalysts.

A. Solbakken (*10*), using the 980 silica–alumina as the catalyst for the same isopentane cracking reaction in the same reactor system and using the same analysis procedure, compared catalyst cracking activities. The activities of the CREX and CREY catalysts were about 20 times that of the amorphous silica–alumina. The activity of the USY catalyst was about five to ten times that of the silica–alumina. Consequently, in the main work that follows 1 g of CREX or CREY catalyst was used to achieve the same hexadecane cracking percentage (about 34%) as 23 g of silica–alumina used by Hightower *et al.* Four grams of USY was used and its activity was almost twice as large (60%) as that of 23 g of silica–alumina.

The results of the final set of experiments appear in Fig. 2. For these cracking runs, a fresh sample of CREX was used each time; the pretreatment conditions were varied. The results clearly show that the highest activity (again measured as percentage of isopentane conversion after 10 min) is obtained when the catalyst is warmed only to the reaction temperature, 440°C. The lowest activity results when the temperature is raised to 520°C and then lowered to the reaction temperature. The results at 490°C were intermediate. No great differences are noted when dry air was used instead of wet air; no great differences are noted when the time of the wet or dry air passing over the catalyst is changed from 1 to 8 hr. Consequently, in the main work, the following pretreatment conditions were used: The samples were evacuated and heated slowly to the cracking temperature and then heated to about 495 to 500°C with dry air flowing over the catalyst for about 10 hr.

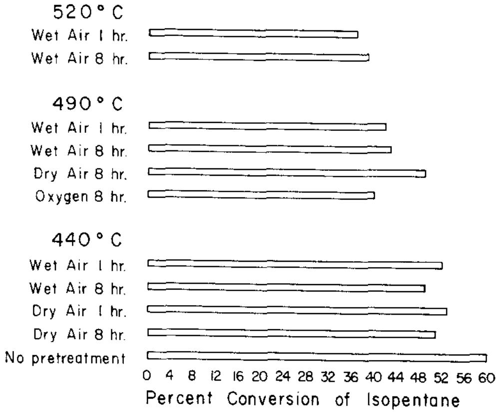

FIG. 2. Effect of pretreatment on the activity of CREX for the catalytic cracking of isopentane.

TRACER EXPERIMENTS: HEXADECANE CRACKING

Since the main idea of this set of experiments was to extend to zeolites the previous work on hexadecane cracking done in this laboratory by van Hook (*7*), Hightower (*8*), and Bartley (*9*), the experimental system and details were kept the same as theirs wherever possible. However some new equipment and techniques were used, and in some areas where problems had occurred improvements were attempted.

Experimental

The all-glass flow system used to crack the hexadecane was very similar to the earlier systems, though it was newly constructed. One helium stream (I), regulated at 158 cm^3/min, bubbled through warm thermostated hexadecane and carried it through heated lines to the reactor. The other helium stream (II), regulated at 12 cm^3/min, carried the tracer, propylene or toluene, and joined with the helium-I-hexadecane stream. For 25 min the mixed gases then passed through the reactor, which was heated to 372°C and, together with the products, were carried to traps, A and B, each in a liquid nitrogen bath. For an additional 15 min helium streams I and II bypassed the tracer and hexadecane injectors but otherwise passed through the entire system to sweep all reactants and products into the traps.

Most of the collected hydrocarbons were in the first trap. A distillation at room temperature initially and at about 100°C finally resulted in the higher-boiling components remaining in trap A and the lower-boiling ones being found in trap B. The gases volatile at room temperature from traps A and B were then collected in a previously evacuated 1-liter bulb. The two traps with liquid were weighed separately and their contents transferred to small vials which were stored at 0°C. The coke produced was burned off the catalyst by passing air through the reactor at about 500°C. The resulting gases then passed through an 800°C oven containing a platium gauze. The carbon dioxide formed bubbled through two traps in series containing saturated barium hydroxide solution and was collected as barium carbonate.

The gas and liquid A and liquid B products were qualitatively and quantitatively analyzed with a Beckman GC-2A, thermal conductivity gas chromatograph using columns containing OPN Porasil-C or DEGS (diethylene glycol succinate) at several temperatures. The quantitative analysis was done by measuring the areas (height times width at half-height) of all peaks. A technique by W. A. Dietz (*11*), involving relative thermal conductivity response factors of various substances, was used to convert areas to mole and/or weight percent. It is important to note that a separate qualitative and quantitative analysis had to be done for each different catalyst. However, for each catalyst the product distribution results from the propylene run were also used for the toluene run.

The eluted, separated components were collected and then individually oxidized and counted in a static counting system using Baird Atomic Co. equipment, or they passed directly into an oxidation chamber and then into a flow-through scintillation counter, Packard Model 3022. The output from the two counting methods was correlated by putting identical samples through each procedure. The barium carbonate, from the coke, was acidified and the radioactive carbon dioxide counted in the scintillation counter. In all cases, carbon dioxide was the only substance ever counted.

Chemicals

The hexadecane used was obtained from Matheson, Coleman, and Bell, labeled 99%-olefin free. It was washed several times with concentrated H_2SO_4 until no color appeared in the acid, and then washed and dried. The cetane was only warmed during the time of the runs, and an atmosphere of helium was always left in the bubbler. With these precautions the hexadecane appeared to remain pure.

The radioactive [1-^{14}C]propylene was purchased from New England Nuclear, NEC 199, Lot 212.016, 0.25 mCi, 2.1 mg, 5.0 mCi/mmol. For run 16 (CREX) the tracer was diluted to 0.35 mCi/mmol. For all later runs, the activity used was 0.36 mCi/mmol.

The [1-^{14}C]toluene (ring label) was also purchased from New England Nuclear, NEC-103, Lot 345.199, 0.25 mCi, 2.5 mg, 9.4 mCi/mmol. This tracer was diluted to 0.15 mCi/mmol.

The CREX, CREY, and USY samples were all obtained from W. R. Grace Co. in powder form. CREX was labeled standard "A," sample number 4482-42. The area was 831 m^2/g after 2 hr at 1000°F. Elemental analysis was reported as: SiO_2, 38.34%; Al_2O_3, 24.56%; rare earth oxide, 29.80%; Na_2O, 0.14%.

CREY was standard "B," sample number 4448-33. The area was 831 m^2/g after 2 hr at 1000°F (*13*). Elemental analysis was given as: SiO_2, 60.57%; Al_2O_3, 18.19%; rare earth oxide, 17.90%, Na_2O, 0.062%.

Details concerning the preparation and properties of USY may be found in the article by McDaniel and Maher (*6*).

The Davison #980 silica–alumina commercial cracking catalyst was in the form of $\frac{3}{16}$-in. cylindrical pellets. Elemental analysis was given as: Al_2O_3, 13.21%; Fe, 0.03%; sulfate, 0.30%; Na_2O, 0.02%; SiO_2, 86.44% by difference. Hightower found the surface area to be 388 m^2/g and the pore volume to be 0.368 cm^3/g with an average pore radius of 18.95 Å (*8*).

The lanthanum-exchanged silica–alumina (runs 23–24) and ammonium-exchanged CREX (run 25) were prepared using normal exchange procedures.

Results and Discussion

The product distribution is given as moles of the particular substance per 100 moles of cetane cracked. The distributions of products from the six catalysts included in the present work are summarized in Fig. 3. All compounds with the same carbon number are grouped together. Hightower's results using silica–alumina catalyst 980 are also included. Connecting lines are drawn in the figure to emphasize the two general patterns for silica–alumina and zeolites, with silica–alumina (exchanged with lanthanum ions) and CREX chosen as the two examples. The obvious differences are that smaller amounts of C_3–C_5 compounds and more C_7–C_9 compounds are formed when a zeolite is the catalyst. Hightower's results were very similar to the present work, except for the large unexplained difference in the C_4 compounds.

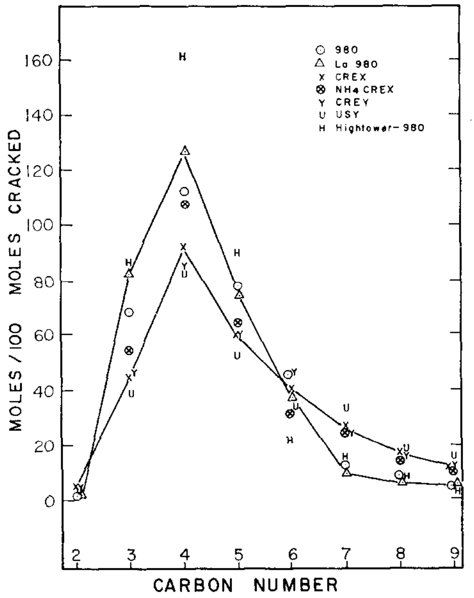

Fig. 3. Product distribution by carbon number for zeolites and amorphous silica–alumina cracking catalysts for cracking cetane.

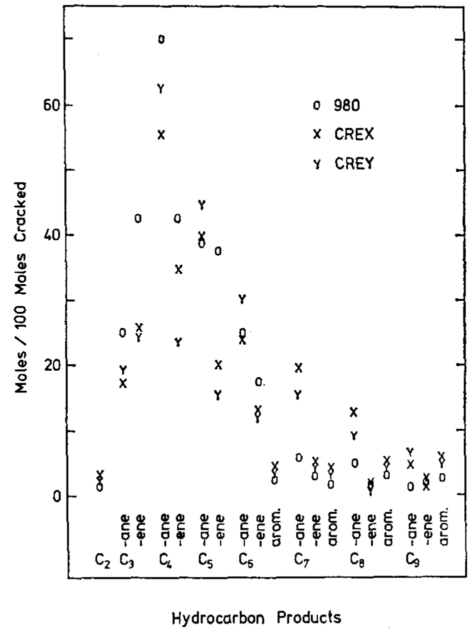

Fig. 4. Product distribution of alkanes, alkenes, and aromatics in cracking cetane over zeolites and amorphous silica–alumina catalysts.

Another plot, Fig. 4, also shows the product distribution (moles/100 moles cracked) vs carbon number but is broken down into alkanes, alkenes, and aromatics. The results from three representative runs are shown: silica–alumina, CREX, and CREY.

Several interesting points might be noted. For compounds with more than three carbon atoms the alkane:alkene ratio is greatest for the zeolites, especially for the Y zeolites. This is expected since Y zeolites are known to be good hydrogen transfer catalysts. The ratio is much smaller for the silica–alumina catalysts, particularly for C_5 compounds and higher.

The larger amount of C_7–C_9 compounds produced over zeolite catalysts as compared to silica–alumina catalysts seems to reflect primarily the large number of alkanes, although there are also more aromatics and to a lesser extent more alkenes.

The radioactivity measurements are given as α values and as percentages of the total activity. The hexadecane cracks and forms primary products, a, which then undergo secondary reactions to form the products, i,

$$C_{16}H_{34} \rightarrow a \rightarrow i.$$

If a small amount of radioactive a, a^*, is added to the cetane, the importance of this particular intermediate a in undergoing secondary reactions is given by the amount of radioactivity incorporated in each of various products i. The α value is defined as:

$$\alpha_a{}^i = \left[\frac{\text{specific (volume) activity of } i}{\text{specific (volume) activity of } a}\right]_{(\text{at exit})}. \tag{1}$$

As an example, if the α value is large, the intermediate a is important in the formation of i. The percentage of the total radioactivity in each product is also reported.

The α values averaged by carbon number for all the propylene tracer runs are plotted on a semilogarithmic scale in Fig. 5. By definition the α value for propylene is one ($\alpha = 1$) for each run. Hightower's results using radioactive propylene are also included.

As expected the results of the current and earlier experiments using #980 silica–alumina are strikingly similar except for propane. There is no known reason for the propane results to differ so much. It is interesting to note that the two runs using silica–alumina (20 and 23) give the same high propane α value, 5.5. This would imply that the present work is self-consistent. The result could be explained if there were a few percent of radioactive propane impurity in the active propylene in the present work. However gas chromatographic analysis showed no propane; analysis of the radioactivity showed at most 1% propane in the radioactive form. This is too small to account for the high α values for propane compared to Hightower's work.

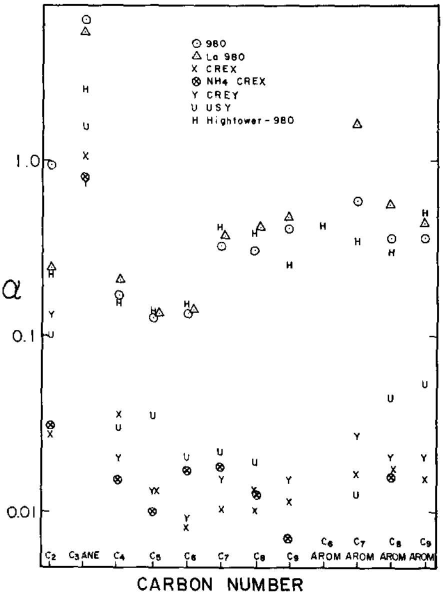

FIG. 5. α Values for tracer experiments with radioactive propylene over zeolites and amorphous silica–alumina cracking catalysts.

The zeolite results are similar to each other, as seen in Fig. 5. The zeolite α values for compounds larger than C_3 are only about one-tenth of those from the silica–alumina runs. The α values for the aromatics are slightly larger than for the nonaromatics. Unlike the silica–alumina results, the α values for the C_7–C_9 hydrocarbons on the zeolites are not larger than the C_4–C_6 values.

Table 1 shows the percentage of radioactivity of selected groupings of products

TABLE 1

Percentage of Total Radioactivity for Each Propylene Run

Compound(s)	CREX-16	CREY-19	USY-21	NH_4CREX-25	980-20	La980-23	Hightower-980
$<C_3$	0.24	0.71	0.46	0.14	0.61	0.16	0.5
C_3-ane	37.67	32.02	43.69	33.06	64.24	55.84	39.5
C_3-ene	53.96	57.31	42.20	58.49	16.72	22.56	30.7
C_4–C_5	4.03	5.61	7.85	4.86	11.84	14.83	18.8
$>C_5$	2.00	2.05	2.68	1.71	4.64	3.95	5.2
Aromatics	0.38	0.52	1.76	0.07	1.31	1.96	1.8
Coke	1.73	1.77	1.38	1.65	0.64	0.98	3.5
Cracking (%)	36.4	31.3	60.5	32.6	36.8	33.0	34.5

from all of the runs using propylene as tracer. Again the two silica runs, 20 and 23, are quite similar to each other and quite different from the zeolite runs. One notices that rows 1, 4, 5, and 6 for the current runs 20 and 23 are similar to the results of Hightower. However Hightower's results show slightly more activity remaining as propylene, much less occurring in the propane, and much more in coke. In fact, runs 20 and 23 have a smaller percentage of the total radioactivity in the coke than any of the zeolites, whereas Hightower's runs show the largest coke percentage of activity of all. The zeolite results are all similar to each other. They differ from the silica–alumina runs primarily in that much more radioactivity remains in the unreacted propylene. Therefore in Table 1 all the other percentages are smaller for the zeolites than for the silica–alumina runs, except for the coke. In general the run 21 (USY) results are intermediate between the two extremes, apparently because of the much larger cracking percentage in this run.

In seraching for a possible explanation of the low α values for the zeolite catalysts, we made some test runs on catalyst 980 after it was exchanged with lanthanum ions and on a zeolite catalyst exchanged with NH_4^+ ions. As is evident from Figs. 3–5 and Table 1, the exchanged catalysts were substantially the same in regard to their α values for the propylene as were the original samples. Accordingly the low α values on the zeolites are not caused by the presence of exchanged lanthanum ions in the zeolites.

To explore further by tracer expeiments the differences between the behavior of zeolite catalysts and amorphous silica–alumina catalysts, radiactive toluene was added to the stream of cetane and passed over the catalyst. The results tabulated in terms of α values are shown in Table 2. The percentages of the radioactivity built into the various selected groups of compounds are given in Table 3. It is apparent that relatively little of the toluene was incorporated into products over the various catalysts, the average being about 9% into compounds or coke over the zeolites and 12.6% over the amorphous catalyst.

The experiments on toluene clearly show that there was little difference between the radioactivities of products over zeolite catalysts as compared to the amorphous silica–alumina catalyst. The percentage of the radioactivity incorporated into the C_8–C_9 aromatics by the toluene is somewhat smaller for the zeolites as compared to the amorphous lanthanum-exchanged 980 catalyst. For benzene and coke it is considerably larger for the zeolites than for the amorphous catalysts. With few exceptions, the α values are somewhat larger for the toluene runs or the zeolites than on the amorphous catalyst.

The question naturally arises as to why the α values for the propylene are so low

TABLE 2

α Values for Toluene Runs

Compound	CREX-17	CREY-18	USY-22	La980-24	Hightower-980
Benzene	0.005	0.0025	—	0.0006	0.0006
Toluene	1.000	1.000	1.000	1.000	1.000
Ethylbenzene					
p-Xylene	0.021	0.028	0.026	0.016	0.019
m-Xylene					
o-Xylene					
n-Propylbenzene	0.026	0.016	0.024	0.018	0.032
1,3,5-Trimethylbenzene	0.026	0.029	0.022	0.016	0.004
1,2,4-Trimethylbenzene	0.026	0.003	0.005	0.007	—
1,2,3-Trimethylbenzene	—	0.013	0.01	0.02	—
Others	0.026	0.025	0.02	0.014	—
Coke	0.0004	0.0009	0.0003	0.0001	—

and the build-in of radioactivity in the cracking products so limited. One is at first tempted to believe that the radioactive propylene cannot equilibrate in the pores with the propylene formed by decomposing cetane. This could result from the "traffic jam" attending the inflow of cetane into the 9-Å openings of the zeolite cages and the outflow of products. Against this explanation are two bits of evidence. In the first place, toluene, a larger molecule than propylene, shows α values substantially as high on the zeolites as on the amorphous catalysts. Toluene must therefore be penetrating to the reaction sites. One would therefore expect propylene to be able to do likewise. The second bit of evidence comes from a consideration of coke formation during the propylene runs. As Table 1 shows, there is on an average twice as much radioactivity in the coke from propylene runs on zeolites as from similar runs on catalyst 980. Furthermore, apparently the coke is formed more from propylene in the zeolite runs than from the other olefins. Table 4 presents a calculation of the α values per carbon atom for the olefins and propane in the zeolite runs compared to the runs on catalyst 980. It will be noted that on an average the α value per carbon atom for catalyst 980 is about the same, within a factor of two, for the coke and for the

TABLE 3

Percentage of Total Radioactivity for Each Toluene Run

Compound	CREX-17	CREY-18	USY-22	La980-24	Hightower
Benzene	0.49	0.32	—	0.08	0.0064
Toluene	91.09	89.24	92.3	87.40	95.00
Ethylbenzene					
p-Xylene	2.18	2.69	3.11	3.94	0.63
m-Xylene					
o-Xylene					
n-Propylbenzene	0.74	0.64	0.56	0.78	0.53
1,3,5-Trimethylbenzene	0.58	0.86	0.70	1.16	0.1
1,2,4-Trimethylbenzene	1.65	0.21	0.35	1.12	—
1,2,3-Trimethylbenzene	—	0.52	0.45	1.75	—
Others	2.56	2.40	2.65	3.25	—
Coke	0.71	3.13	0.57	0.54	2.0

TABLE 4

α Values for Coke, Olefins, and Propane (per Carbon Atom)

Compound(s)	CREX	CREY	USY	NH_4CREX	980	La980
Propane	0.34	0.25	0.51	0.25	2.08	1.76
Propylene	0.33	0.33	0.33	0.33	0.33	0.33
Butene	0.0027	0.0062	0.006	0.003	0.041	0.042
Pentenes	0.0016	0.0019	0.008	0.0016	0.024	0.025
Hexenes	0.0013	0.0015	0.003	0.001	0.022	0.018
Coke	0.013	0.008	0.008	0.009	0.025	0.047

olefins. On the other hand the α values for the coke on the zeolites are up to 10 times as great as for the per carbon values for the olefins. Of course we have to remember that the α values are activities per mole of product divided by radioactive content per volume of tracer at the exit. Because of the large volume of propylene and the low percentage of radioactivity in the propylene for the 980 catalyst, the denominator of Eq. (1) is one-fifth as large for the 980 catalyst as for the zeolites. Accordingly, the factor of 10 in the ratio of α values for products in the runs over catalyst 980 to those on the zeolites is mostly to be accounted for by this factor of five. The actual radioactivity per volume of product is only smaller by a factor of two on the zeolite catalysts than on catalyst 980. It seems at the moment that the data here presented are more a reflection of fundamental differences in the nature of the surface reactions on the zeolites as compared to the amorphous catalysts. This is not surprising, because, as pointed out, there are striking differences between the products from the zeolites and the amorphous catalysts. Figure 3, for example, emphasizes the shift in the average molecular weight of products to higher figures for the zeolites than for the amorphous catalysts. Furthermore, the zeolites admittedly are better hydrogen transfer catalysts and yield higher alkane to alkene ratios than do the amorphous catalysts (Fig. 4). The toluene apparently behaves about the same on the two types of catalysts with respect to the adding of one or two carbon atoms to form C_8 and C_9 aromatics.

To sum up, it is impossible from the present data to say definitely the extent to which the kinetic or "traffic jam" factor enters into the observed behavior in the propylene and toluene tracer runs, but it seems certain that differences of the types of surface reactions involved is probably a major factor in the low α values obtained for the zeolites in the propylene tracer runs.

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