

Activity, Selectivity, and Deactivation of High-Sodium HY Zeolite

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The effect of deactivation on the activity and selectivity of (very high) Na⁺ content HY zeolite catalysts was studied in a pulse microreactor equipped with a thermogravimetric analysis unit (TGA). Cumene was used as the reactant. The Na⁺ level studied was from 3.2 to 11.8% of Na₂O. As the Na⁺ content decreases, the acidity of the zeolite increases and deactivation decreases. The effect of coke level on selectivity to benzene, toluene, ethylbenzene, dimethylbenzene, ethyltoluene, cymene, and diisopropylbenzene depends on the Na⁺ content. For example, the selectivity to benzene, the major aromatic formed by the fresh catalyst, decreases with increasing coke level and Na⁺ level, while the selectivity to ethyltoluene increases under the same conditions. A maximum in selectivity with coke level is obtained for most other products. At intermediate Na⁺ levels (around 7% Na₂O), ethylbenzene shows a maximum in selectivity while cymene passes through a minimum. The maximum coke deposition and the coke level for the maximum incremental coke deposition are two important parameters that distinguish conversion and selectivity patterns.

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INTRODUCTION

The Y-type zeolite, largely used as a cracking catalyst, is synthesized in sodium form and the sodium is then mostly replaced with H⁺ and/or a variety of other cations. Removal of Na⁺ ions from the zeolite structure occurs sequentially. The weakly bound ions and those closer to the Y supercage are preferentially removed. Possible location of Na⁺ ions in and around the sodalite structure have been classified as Types I, I', II', and II, in increasing order of ease of removal (1).

The catalytic activity, selectivity, and coking behavior of an HY zeolite are affected by the residual Na⁺ content as well as other physical properties, such as Si/Al ratio. Na⁺ is considered a poison to zeolite acidity and activity. Beyerlein *et al.* (2) and Fritz and Lunsford (3) have proposed that one Na⁺ neutralizes three to five framework Brønsted acid sites. A zeolite with a low Na⁺ content usually has a higher cracking activity than one with a high Na⁺ content.

However, the effect of Na⁺ on the cracking reaction is complex; more than just acidity and activity are affected. In many cases,

product selectivity is an important factor to be considered. For a fresh catalyst, Pine *et al.* (4) note that Na⁺ affects selectivity at levels of less than 1% (as Na₂O). Madon *et al.* (5) have reported beneficial effects of Na⁺ in fluid catalytic cracking. Very high acid strength may lead to excessive formation of coke and low-molecular-weight gases.

Cumene cracking is a useful probe reaction for Y zeolites, since sites of medium strength are used (3). Benzene and propylene are the major products, but not the only ones; Corma and Wojciechowski (6) have identified various disproportionation and other products formed in smaller amounts by the fresh catalyst.

In this paper, we report the quantitative effects of Na⁺ content on HY zeolite activity, selectivity, and coking in the cracking of cumene. We observe that selectivity changes with Na⁺ level at values much greater than 1% Na₂O for deactivating (coking) catalysts.

EXPERIMENTS

Experiments were carried out in a pulse microreactor. Our setup allows ambient-

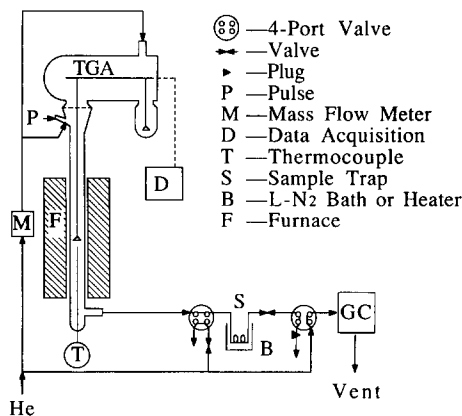


FIG. 1. Experimental apparatus.

pressure operation, efficient collection of products, and higher-pressure transfer to a gas chromatograph (GC) for efficient analysis. Details of an earlier version are provided in Ref. (7). A brief description of changes is given below.

The reaction apparatus is shown in Fig. 1. The reactor is a thermogravimetric analysis unit (TGA) Cahn System 113. Pulses of cumene are injected in a stream of heated helium carrier gas. Back diffusion of the reactant to the recording and measuring head is minimized by having a separate helium stream flow through the head and into the Pyrex reactor tube through a small hole. The unit is a flow-through type, with an external oven. The outlet stream leaving the catalyst flows through a collector, where condensable gases are captured at liquid-nitrogen temperatures (-195.8°C) by suitable manipulation of four-port valves. After a suitable time, when all products are considered collected, the liquid-nitrogen reservoir is replaced by a heating mantle, and the temperature of the collector contents is raised to 177°C . At this temperature, the collector contents are in the vapor phase and are flushed by high-pressure He to the GC for product analysis.

The catalysts used are Y zeolites with different amounts of Na^+ . The physical properties of the catalysts are listed in

Table 1. Cumene from Aldrich with purity of greater than 99% was used. The He carrier gas was from West Virginia Welding with a minimum purity of 99.5%. A Varian 3300 GC with FID and a $10\text{ ft} \times \frac{1}{8}\text{ in.}$ packed column with 10% SP-2100 on 100/120 Supelcoport was used for product analysis.

The reactions were carried out at 500°C and ambient pressure, with a helium flow rate of 100 ml/min . The catalyst samples (about 5 mg) were heated at these conditions for 3 h before the reaction. The balance was tared before each injection of the pulse, and the time interval between the pulses was 40 min. The pulse size was $5\text{ }\mu\text{l}$.

DATA ANALYSIS

The method we used is based on GC areas and an aromatic-ring balance. The aromatic ring remains unaltered in the cracking of alkylaromatics (6). If all the components with aromatic rings can be collected and determined, the amount of cumene that passed through the reactor can be determined. The lightest aromatic molecule is benzene. Benzene is a liquid at room condition and it can be easily and quantitatively trapped in the collector by the liquid nitrogen; higher-boiling compounds would even more assuredly be trapped.

To determine the amount of aromatics collected, the products of the reaction were

TABLE 1
Physical Properties of NaHY Zeolites

Sample No.:	1	2	3	4
% Na_2O	11.8	10.5	7.3	3.4
% Na^+ /unit cell	48	42	28	12
% N	<0.01	<0.01	0.02	0.02
Surface area (m^2/g)	947	985	914	898
TPD activity ($\mu\text{mol/g}$)	1130	1102	1876	2302
NH_3 desorption ($\mu\text{mol/g}$)	473	544	946	1913

Note. Si/Al = 5.0; unit cell size = 24.65 \AA .

TABLE 2
Products Identified

No.	Compounds	No.	Compounds
1	Propylene (PRO)	6	<i>n</i> -Propylbenzene (NPB)
2	Benzene (BEN)	7	Ethyltoluene (ET)
3	Toluene (TOL)	8	Cymene (CY)
4	Ethylbenzene (EB)	9	Ethylpropylbenzene (EPB)
5	Dimethylbenzene (DMB)	10	Diisopropylbenzene (DIB)

first identified and are listed in Table 2. Products with molecular weights less than that of benzene show only one peak in the GC analysis. The products are lumped into "collected propylene" in our analysis. Some lighter products may escape from the collector. These can be quantified on a propylene-equivalent basis and are used in the selectivity calculations. They are denoted by "propylene equivalents." The sum of propylene equivalents and collected propylene is termed the "total propylene equivalents." Since the reactant and all the products, except propylene, contain an aromatic ring, the conversion and the selectivities can be calculated as shown below. If N_i and M_i are the number of moles of component i in the collector and the molecular weight of i , respectively, then

$$\text{Moles of aromatic ring collected} = \sum N_i \quad (i \neq \text{propylene}) \quad (1)$$

$$\text{Moles of cumene before reaction} = \sum N_i \quad (i \neq \text{propylene}) \quad (2)$$

$$\text{Conversion, } X = 100 \left\{ 1 - \frac{N_{\text{cumene}}}{\sum N_i (i \neq \text{propylene})} \right\} \quad (3)$$

$$\text{Weight of cumene before reaction} = M_{\text{cumene}} \sum N_i (i \neq \text{propylene}) \quad (4)$$

$$\text{Weight of collected effluent} = \sum (N_i M_i) \quad (5)$$

$$\text{Weight of gas lost} = M_{\text{cumene}} \sum N_i (i \neq \text{propylene}) - \sum (N_i M_i) \quad (6)$$

$$\begin{aligned} &\text{Moles of gas lost} \\ &\text{(propylene equivalent)} \\ &= \frac{M_{\text{cumene}} \sum N_i (i \neq \text{propylene}) - \sum (N_i M_i)}{M_{\text{propylene}}} \quad (7) \end{aligned}$$

$$\begin{aligned} &\text{Selectivity to species } j, S_j \\ &= 100 \left\{ \frac{N_j}{\sum N_i (i \neq \text{propylene}) - N_{\text{cumene}}} \right\} \quad (8) \end{aligned}$$

$$\begin{aligned} &\text{Selectivity to total propylene equivalents} \\ &= \frac{M_{\text{propylene}} N_{\text{propylene}} + M_{\text{cumene}} \sum N_i (i \neq \text{propylene}) - \sum (N_i M_i)}{M_{\text{propylene}} \{ \sum N_i (i \neq \text{propylene}) - N_{\text{cumene}} \}} \quad (9) \end{aligned}$$

Equations (3), (8), and (9) are the required relations. Equation (8) is valid for collected propylene but not propylene equivalents. Equation (9) adds the selectivities for collected propylene and propylene equivalents. It is important to note that the results obtained from the aromatic-ring balance are not affected by the loss of lighter-than-benzene products that are not wholly trapped in the sample collector at the liquid-nitrogen temperature. Again because of the aromatic-ring balance, the conversion and the selectivities obtained do not take into account the cumene that has been converted to coke. Hence conversion and selectivity values are on a coke-free basis. This implies that the coking reaction occurs in parallel with the other reactions.

RESULTS AND DISCUSSION

Deactivation

The deactivation of zeolite catalyst in this case is caused by coking. Selected activity and coke level data are shown in Table 3 as a function of cumene injection for Zeolites 1 and 4.

The coke depositions for Zeolites 1 and 4 are plotted versus cumulative cumene injected in Fig. 2. Curves for Zeolites 2 and 3 lie in between these two curves. The sigmoid-

TABLE 3
Typical Product Distributions of Reactor Effluent

Pulse	Weight percentage of major components ^a								Coke on catalyst (%)
	Gas	PRO	BEN	TOL	DMB	Cumene	ET	CY	
For Zeolite 1									
1	2.57	0.90	6.46	0.00	0.02	89.92	0.14	0.04	0.17
2	2.35	1.02	6.30	0.01	0.02	89.89	0.29	0.13	0.61
5	1.77	0.88	4.99	0.04	0.11	90.00	1.01	0.23	6.18
10	0.35	0.25	1.11	0.04	0.10	95.17	2.86	0.11	18.42
13	0.14	0.08	0.42	0.01	0.06	97.98	1.29	0.04	19.82
For Zeolite 4									
1	3.64	3.68	13.61	0.01	0.00	78.88	0.11	0.03	0.08
2	4.27	2.44	12.45	0.01	0.07	80.56	0.14	0.04	0.33
5	4.12	2.53	12.39	0.03	0.10	80.17	0.36	0.15	1.80
10	3.70	1.97	10.55	0.08	0.14	81.39	1.52	0.21	10.29
13	1.93	1.10	5.65	0.02	0.11	88.80	2.15	0.13	14.26

^a See Appendix.

dal shape and the asymptote suggest an autocatalytic mechanism for coking. A coking model has been developed and reported (8). This coking behavior indicates that using cumulative reactant or time as the independent variable to analyze activity and selectivity is not appropriate. In the following analysis, therefore, the cumulative coke deposition is used as the independent variable.

The autocatalytic coking mechanism indicates, and experimental data verify, that the incremental coke deposition (net coke for-

mation after each pulse) or coking rate starts from zero for the fresh catalysts, goes through a maximum (the maximum incremental coke deposition, MICD), and then decreases to zero. This is shown in Fig. 3 for the four zeolites. To illustrate the physical significance of MICD, the value of MICD is indicated in Fig. 3. for Zeolite 4 only. Note the rapid drop in coking rate after MICD.

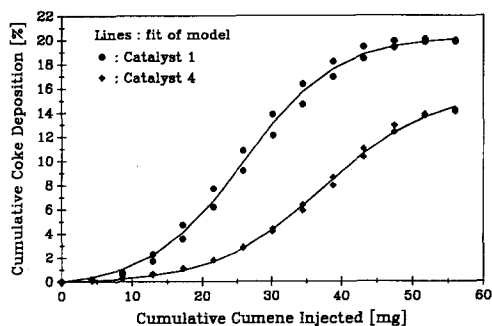


FIG. 2. Coke deposition as a function of cumene injected in pulse microreactor. Lines are fit to the model of Ref. (8).

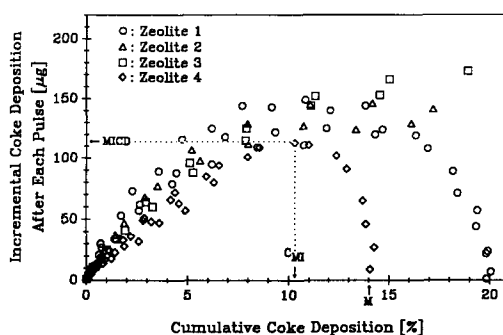


FIG. 3. Incremental coke deposition (per pulse) for Catalysts 1-4 as a function of cumulative coke on the catalyst. The maximum incremental coke deposition (MICD) represents the maximum of the curve, and C_{MI} is the corresponding coke level. M represents the maximum coke deposition. MICD, C_{MI} , and M are shown for Catalyst 4.

TABLE 4
 M and C_{MI} for the Four Zeolites

Zeolite	Na ₂ O%	M	C_{MI}
1	11.8	20	14
2	10.5	>20	~15
3	7.3	≧20	>18
4	3.2	14	11

The coke level for MICD (C_{MI}) and the maximum cumulative coke deposition (M) on the zeolite are two important parameters in describing coking and in analyzing activity and selectivity, as shown in the following section. From the coking model (8), C_{MI} can be related to the balance between uncoked sites (where coke can deposit) and coked sites (which autocatalyze coke deposition). Again from (8), M is a measure of ultimate coke capacity. C_{MI} is greater than one-half of M because coke is deposited in multiple layers on the catalyst. Then the coke formed at levels greater than C_{MI} is more likely to be multilayered coke than the coke formed at lower coke levels.

M and C_{MI} are also indicated for Zeolite 4 in Fig. 3. Although the experiments for Zeolites 2 and 3 were not carried out to sufficiently high coke levels to show the values of M and C_{MI} for these catalysts, the values can be estimated from the data available and the coking model (8). The M and C_{MI} values for the four zeolites are listed in Table 4 along with Na⁺ content.

There is clearly a nonlinear relationship between these coke values and the Na⁺ level. For Na⁺ content between 12 and 7% Na₂O, M and C_{MI} increase with decrease of Na⁺, indicating that more coke can potentially be deposited on a catalyst with a lower Na⁺ content. However, M and C_{MI} decrease when Na⁺ content is further reduced (to 3% Na₂O). We show below that other significant changes in zeolite properties occur between 7 and 3% Na₂O. This phenomenon was also reported by Chen *et al.* (9), where a change point of about 4% Na₂O was observed for

microcalorimetric studies of the acidity of HY zeolites. As Table 1 indicates, the change from 7 to 3% Na₂O implies a change from 28 to 12 Na⁺/unit cell. These 12 Na⁺ ions are probably all of Type I, i.e., lying in the center of the hexagonal prism, away from the supercage (I).

Activity

The activity of the zeolite catalysts is defined as the conversion of cumene (on a coke-free basis). The activity for the four catalysts decreases relatively slowly and approximately linearly with an increase of cumulative coke deposition up to C_{MI} . At coke levels higher than C_{MI} , there is a sharper, nonlinear drop in activity with coke level, and the activity tends to zero at M . If C_{MI} is a measure of the shift between "initiation" coke and "propagation" coke, as noted above, then there is a qualitative change in activity loss with a change in the type of coke deposited.

In the linear region, linear regressions were made using

$$X = X_0 - A \cdot C, \quad (10a)$$

where X_0 is the initial activity and A is the gradient of activity loss due to coke. The relative activity is defined as X/X_0 , so that

$$X/X_0 = 1 - B \cdot C. \quad (10b)$$

B is the gradient of relative activity loss due to coke.

The initial activity X_0 is plotted against Na⁺ level in Fig. 4. X_0 increases with a decrease of Na⁺ content for Zeolites 1–3, as one would have expected. However, a further decrease in Na⁺ content (below 7% Na₂O, to Zeolite 4) does not improve the initial activity.

From Table 1, Zeolites 1–3 contain 48–28 Na⁺/unit cell. Decreasing the Na⁺ content from 48 to 28 almost certainly removes only Type II sites, i.e., those outside the hexagonal faces of the supercage (I). These sites apparently influence the initial activity. Decreasing the number from 28 to 12, i.e., removing sites of type II' (inside the hexago-

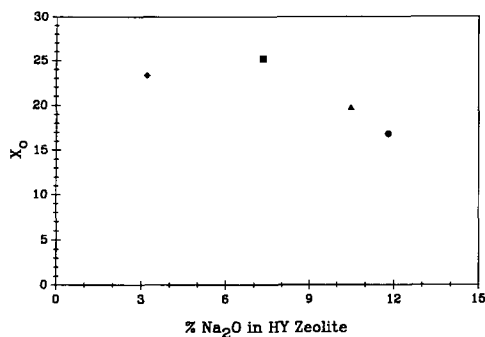


FIG. 4. Initial activity X_0 as a function of Na^+ content.

nal face of the sodalite) and I' (inside the sodalite near the hexagonal prism) apparently does not change the activity to a large extent.

The relative activity X/X_0 is plotted against cumulative coke in Fig. 5. For all Na^+ levels considered here, the slope B decreases with decreasing Na^+ level. The coke level affects the relative activity of a catalyst with a lower Na^+ level less than one with a higher Na^+ level. This suggests that, for a catalyst with a lower Na^+ content, a smaller percentage of sites active for cumene cracking are deactivated by (the same amount of) coke. Decreasing the Na^+ content creates sites relatively resistant to deactivation. In other words, at these coke levels, a decrease in Na^+ content reduces the sensitivity of the catalyst to coke.

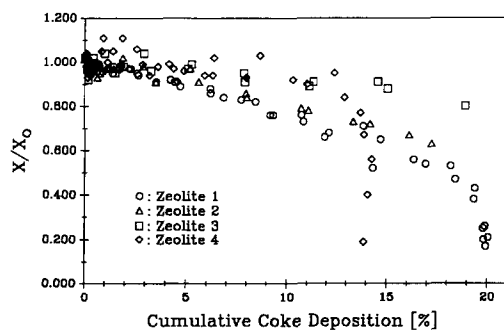


FIG. 5. Relative activity X/X_0 for Catalysts 1-4 as functions of cumulative coke on the catalyst.

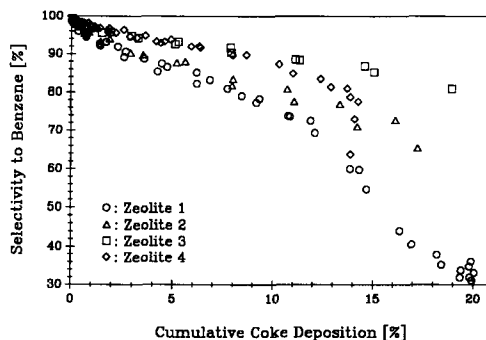


FIG. 6. Selectivity to benzene with Na^+ content and coke level.

Selectivity

a. Selectivity to benzene. The selectivity is coke-free molar selectivity as defined earlier by Eq. (8). The selectivity to benzene for each of the four catalysts is plotted versus cumulative coke deposition in Fig. 6.

The initial selectivity is greater than 99% for all the four catalysts. At these high Na^+ levels, the selectivity of the fresh Y catalyst is independent of Na^+ content, as expected (4). The virtually complete conversion to benzene for the fresh catalysts indicates that the reaction that produces benzene is primary, in Wojciechowski's nomenclature, and that isomerization and disproportionation reactions are negligible.

For deactivating zeolites, there is an initial steep decrease in the selectivity, up to about 1% coke. This is followed by a small, but linear, decrease with increasing coke level. In these regions, the benzene selectivity trend is opposite the trend of incremental coke deposition as functions of coke level; compare Figs. 3 and 6. This suggests that benzene formation and coke deposition run in parallel and that active site suppression affects benzene selectivity.

Another steep decrease is observed after the coke level of C_{MI} , and the selectivity tends to zero at M . The shift in selectivity at C_{MI} can be ascribed to the change in the emphasis of coke deposited, from single layer to multilayer. The active sites for

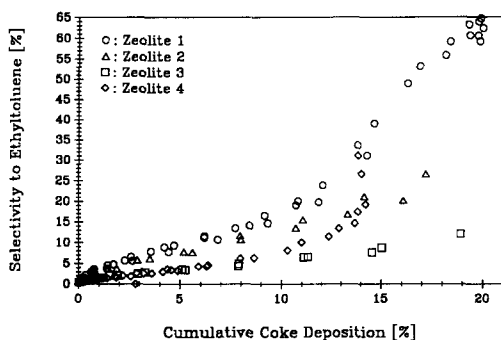


FIG. 7. Selectivity to ethyltoluene with Na^+ content and coke level.

cracking are severely affected by coke formation, relative to the other sites.

The decrease in the selectivity with respect to the cumulative coke deposition is different for the four catalysts. The order of the decrease for the catalysts (before C_{MI} is reached) is: $1 > 2 > 3 = 4$. As shown in Table 1, the Na^+ content for the four catalysts is in the same order for Catalysts 1–3. The lower Na^+ content yields less decreasing benzene selectivity during coking, up to Zeolite 3. Decreasing the Na^+ content further (to Zeolite 4) does not improve benzene selectivity. Similar results have been noted for the magnitude of the overall activity, above. In analogous fashion, therefore, removing Types II and II' Na^+ ions creates cracking sites more resistant to deactivation, at least up to coke level C_{MI} .

b. Selectivity to ethyltoluene. Ethyltoluene (ET) is the largest by-product observed in the reaction, up to 65% for coked Zeolite 1. The relation of the selectivity with cumulative coke deposition (Fig. 7) is different from that of benzene. The selectivity of any of the fresh catalysts is approximately zero, independent of Na^+ level. The selectivity increases with an increase of coke deposition. The increase is linear before C_{MI} is reached and is even greater after that. In the linear region, the order of increase for the four catalysts is: $1 > 2 > 3 = 4$. In other words, the selectivity to ET increases with

decreasing Na^+ level, particularly in the region between 7 and 11% Na_2O .

The increases in selectivity mirror the decreases found for benzene selectivity with coke level and Na^+ level. Hence it would appear that sites active for isomerization to ET are increased (at least in relative amount) during coking, at the expense of sites active for the cracking of cumene. In fact, the absolute amount of ET obtained in the collector increases with coke level up to coke values higher than C_{MI} , and then decreases (Table 3), the maximum occurring at the same coke level as that where the conversion-coke relation becomes nonlinear. ET may be formed early in the process, by isomerization of cumene. ET is then cracked into ethylbenzene, toluene, and benzene, and forms coke precursors. The amount of ET cracked is proportional to the amount of acid sites for cracking. When the acid sites are coked, the cracking ability is limited, and the amount of uncracked ET increases. However, when the active sites for isomerization are also strongly affected by coke, as indicated by the decrease in absolute ET, the overall conversion drops sharply. This suggests that the active sites for cracking are more easily coked than those for isomerization. For coke values larger than C_{MI} , although the active sites for isomerization are also affected, the relative number of isomerization sites (relative to cracking sites) still increases. This explains the much sharper changes in the selectivity after the maximum coke deposition.

c. Selectivity to toluene, ethylbenzene, and diisopropylbenzene. The relations of the selectivities to toluene, ethylbenzene (EB), and diisopropylbenzene (DIB) with cumulative coke deposition for the four catalysts are similar to one another, but different from that for benzene and ET. The similarity indicates that the reactions for producing these three species are closely related. Perhaps the three species have a common intermediate or are formed on the same active site (for disproportionation).

A plot for the selectivity of toluene is

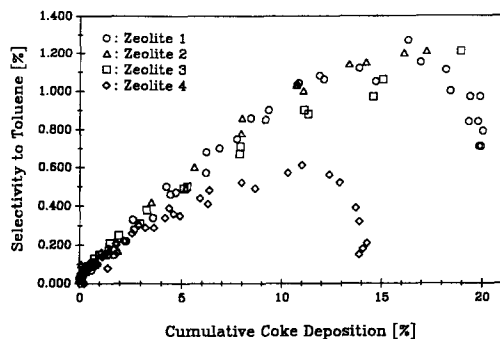


FIG. 8. Selectivity to toluene with Na^+ content and coke level.

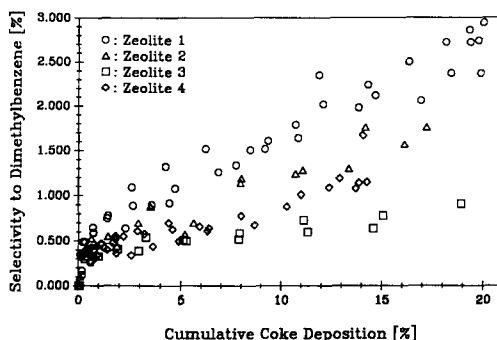


FIG. 9. Selectivity to dimethylbenzene with Na^+ content and coke level.

shown in Fig. 8 as an example. The selectivities increase with the increase of cumulative coke deposition, with an initial value of zero, and then start to decrease. The maximum selectivity occurs at a coke level around C_{MI} for all four zeolites and all three species. In other words, the rate of coking is proportional to the amounts of these species formed. Perhaps the three species are intermediates for, or by-products of, coke formation. The maximum selectivities observed for the three components are 1.2, 2, and 1%, respectively.

For toluene, the selectivity may be decreased by decreasing Na^+ levels. This is the inverse of the effect noted for benzene selectivity. For DIB, no significant change is noted in the selectivity with Na^+ levels. For EB, the selectivity may pass through a maximum for Zeolite 2 (11% Na_2O). This must be related to optimal removal of Na^+ ions in positions I' and II' from the zeolite.

d. Selectivity to dimethylbenzene. The selectivity to dimethylbenzene (DMB) is shown in Fig. 9 and is qualitatively different from those showed earlier. The initial selectivity is zero for the four catalysts, as in the previous section. However, steep increases in the selectivity are observed for the first few pulses, followed by linear increases with cumulative coke deposition. Further, unlike the selectivities to ET, toluene, EB, and DIB, that to DMB shows no qualitative change in behavior with coke deposition

around C_{MI} . Finally, as cumulative coke deposition reaches its asymptotic value M (for Zeolite 4), the selectivity to DMB is perhaps slightly changed. This may indicate that the formation of DMB is related to the absolute amount of coke on the catalysts and not on the types of coke formed.

The magnitude of the selectivity is also affected by the Na^+ level of the catalysts. The selectivity passes through a minimum at a Na^+ content of around 7% Na_2O , corresponding to Zeolite 3. This is the inverse of what is noted for EB, above.

e. Selectivity to cymene. The selectivity to cymene (isopropylmethyl benzene) is shown in Fig. 10. This is different from those discussed earlier. For the fresh catalysts, the selectivity to cymene, though small, is not zero and is independent of Na^+ level.

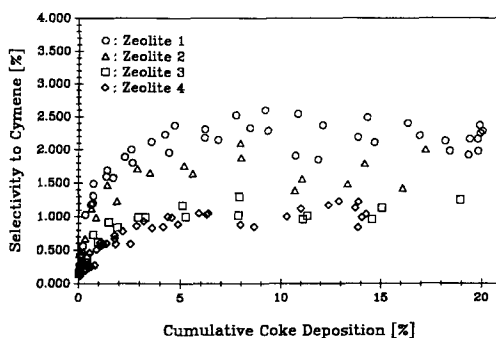


FIG. 10. Selectivity to cymene with Na^+ content and coke level.

For deactivating catalysts, the selectivities increase with an increase in coke level and reach asymptotic values at a coke level of about 5% coke. The maximum selectivity is small, less than 2.5% for all the catalysts. C_{MI} and M have no effect on the selectivity.

The selectivity is affected by the Na^+ level of the zeolites. For Zeolites 1–3, the selectivity decreases with the decrease of Na^+ . Catalyst 4 gives selectivities similar to Zeolite 3. Increasing the number of Na^+ ions of Type II and II' must increase cymene selectivity.

It has been reported (10) that ethylbenzene and cymene are formed from disproportionation of two cumene molecules. The data obtained in this study do not support this for deactivating catalysts because of two reasons. First, the amount of cymene is greater than that of ethylbenzene. Also, the dependence of these selectivities to coke are different. The selectivity to cymene, for example, reaches an asymptotic value ($\sim 2.5\%$ for Zeolite 1) at about 5% coke, whereas the selectivity for EB reaches a maximum ($\sim 1\%$ for Zeolite 1) at C_{MI} and then decreases to zero when M is reached. However, it is possible that EB could crack further, in amounts that increase with coke level. This could yield benzene and toluene, thereby decreasing EB with increasing coke levels.

f. Selectivity to ethylpropylbenzene. The selectivities to ethylpropylbenzene (EPB) are small ($< 0.5\%$) for all four zeolites. The selectivity to this product increases slightly with coke level of the catalysts and then levels off. Because of the low selectivity, no clear trend for the effect of Na^+ level and no sharp changes near C_{MI} are observed. However, a sharp decrease is observed when M is reached. This may suggest that the formation of ethylpropylbenzene is related to coking rate.

*g. Selectivity to *n*-propylbenzene.* The selectivities to *n*-propylbenzene are also very small. The values are independent of coke level and less than 0.05% except for Zeolite

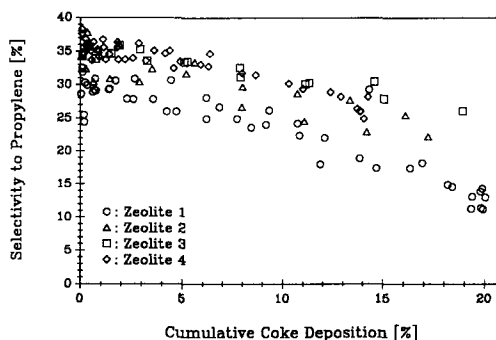


FIG. 11. Selectivity to collected propylene with Na^+ content and coke level.

1, where the selectivity is 0.1% and increases as the coke level approaches M .

h. Selectivity to propylene. The selectivities to collected propylene for the four catalysts are shown in Fig. 11. The nonzero initial values indicates that propylene is a primary product. The general shape of Fig. 11 is the same as that of Fig. 6 (for benzene). Since the selectivities to by-products other than benzene (and also ethyltoluene, which is from isomerization) is small, the major primary gas product (other than benzene) should be propylene. However, it is clear that the amount of propylene observed is much less than the amount of benzene. This may result from losing propylene from the collector, as well as from further cracking of propylene to other lower hydrocarbons, which are more likely to escape from the collector.

The aromatic-ring balance method allows us to estimate the propylene equivalents not in the collector. Adding these to the collected propylene allows us to calculate the selectivity to total propylene equivalents defined in Eq. (8). This selectivity is compared to that of benzene for all catalysts and all coke levels in Fig. 12. All the points lie on a single diagonal line. This confirms the validity of the aromatic-ring balance and indicates that only propylene and cracked propylene products make up the first GC peak and the uncollected gas.

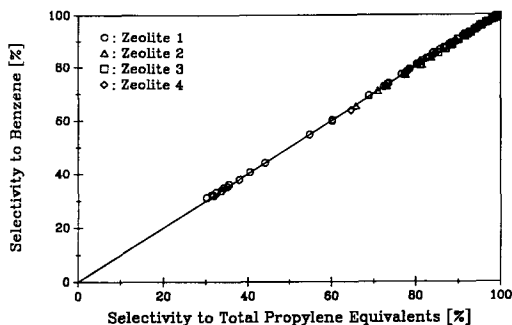


FIG. 12. Comparison of benzene selectivity and selectivity to total propylene equivalents for all catalysts and coke levels.

Reaction Mechanisms

Based on the dependence of selectivity on coke level for each product, a simple reaction mechanism can be proposed as shown in Fig. 13. The cracking of cumene (the main reaction, which produces benzene and propylene), and the isomerization reaction (which produces ethyltoluene) are in parallel with coke formation. The products of isomerization can crack further to give benzene, ethylene, ethane, and methane. However, these reactions are affected by coke because they use the same active sites as coke. The active sites for isomerization may be more resistant to coke.

All other products have an initial selectivity of zero and are dependent on coking rate or coke level. These products are likely formed through intermediates. The formation of toluene, ethylbenzene, and diisopropylbenzene (which are probably produced from disproportionation reactions) is similar to coke formation. These products, therefore, may be produced from the same intermediates and reactions as that for coke. The amounts of cymene, ethylpropylbenzene, and dimethylbenzene produced depend on coke level. These products are probably formed by interaction of the intermediates and coke.

SUMMARY AND CONCLUSION

The Na^+ content of HY zeolites affects zeolite cracking activity and selectivity. A

zeolite with a lower Na^+ content shows higher acidity and slower deactivation. However, for activity and selectivity, the effect of Na^+ content depends on the range of Na^+ content. For catalysts with 7–12% Na_2O (for Zeolites 1, 2, and 3), the coking rate, maximum coke deposition (M), and the initial activity increase with the decrease of Na^+ level. But for the catalysts with smaller Na^+ content (for Zeolite 4, 3% Na_2O), the coking rate and the value of M are much smaller than those for higher Na^+ levels, and the initial activity is lower than that for Zeolite 3.

The effect of Na^+ content on the selectivity depends on the nature of the product. The selectivity to benzene increases with a decrease of Na^+ content below Zeolite 3, and that to ethyltoluene increases with an increase of Na^+ . The selectivity to toluene increases with the increase of Na^+ content. The selectivity to EB shows a maximum between Zeolites 2 and 3. The selectivities

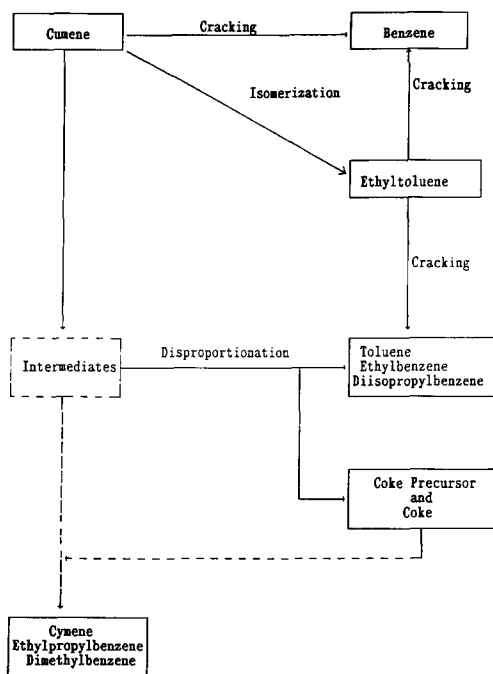


FIG. 13. Proposed mechanisms for coke and product formation.

to DIB and EPB and *n*-propylbenzene are small, and the effect of Na⁺ content is not clear. The cymene selectivity, and that to DMB, may pass through a minimum between Zeolites 3 and 4.

Zeolites 2 and 3 seem to play pivotal roles in selectivity behavior. The corresponding Na⁺ ion levels may be related to the occupation of Type I (I') and II (II') sites in the zeolite lattice.

Now consider the effects of coke level on selectivity. The difference in the relationship between the by-product selectivities and the cumulative coke deposition suggests that the by-products may be formed by different mechanisms. The selectivities to toluene, EB, and DIB show the same trend with increasing cumulative coke as that for coking rate or incremental coke deposition; Fig. 3. This may indicate that the formation of these compounds is closely related to coking. The selectivity to ET shows a rapid increase after C_{MI} is reached. This suggests that ET does not undergo further cracking after a certain coke level. The selectivity of cymene is constant after relative small coke levels, whereas that for DMB appears to increase monotonically with coke.

The proposed mechanism of coke formation and product formation is consistent with these results.

In summary, the selectivity and activity of the high-sodium HY zeolites are influenced by C_{MI} , the coke level corresponding to a balance between initiation and propagation coke, and also by the distribution of Na⁺ ions between the various allowable positions in the zeolite lattice.

APPENDIX: NOMENCLATURE

A	Gradient of activity loss (%/%)
B	Gradient of relative activity loss (1/%)
BEN	Benzene
C_{MI}	Coke level for MICD (%)
CY	Cymene
DMB	Dimethylbenzene

ET	Ethyltoluene
M	Maximum cumulative coke level (%)
M_i	Molecular weight of component <i>i</i> (g/mol)
MICD	Maximum incremental coke deposition after each pulse (μ g)
N_i	Number of moles of component <i>i</i> (mol)
NPB	<i>n</i> -Propylbenzene
PRO	Propylene
S_i	Selectivity to component <i>i</i> (%)
TOL	Toluene
X	Activity or conversion of cumene (%)
X_0	Initial activity or conversion of cumene (%)

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