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Analysis of coupled deactivation effects: Interaction of sodium and coke in cracking over zeolites

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Abstract

Zeolites can deactivate by coke laydown and by poison deposition. Here we consider a simple reaction, the cracking of cumene, over a simple zeolite, type Y, as deactivated by coke deposition and the presence of sodium. We show that the effect of coke level and sodium level can be treated in a unitary manner. This allows the relative magnitudes of coking and poisoning to be quantitatively compared. By coupling this information with what is known about the structure of poisons on active sites, details can be obtained regarding the structure of coke on the active site.

Keywords: Coking; Poisoning; Zeolite Y; Cumene cracking

1. Introduction

Deactivation of acid catalysts such as zeolites occurs most rapidly by the deposition of coke on an active site, but can also occur by the adsorption of poisons. The coke and the poison can affect the same type of active site, or a different type of active site. Hence either coke, or poison, or both, can affect the activity as well as the selectivity of the catalyst.

In an earlier work [1], we reported on the effect of deactivation on the activity and selectivity of NaHY zeolite for cumene cracking. The Na^+ ion is considered a poison to the acidity, and hence the activity, of zeolites [2,3]. For a fresh catalyst, the amount of Na^+ influences selectivity, but only when levels are less than 1% (as NaO) [4]. However, for a catalyst deactivated by coke, we found [1] that the amount of Na^+ and the amount of coke influence the activity and selectivity of the catalyst at Na^+ levels as high as 12% (as NaO).

We recently became aware of treatments which indicate how simultaneous coking could be analyzed in conjunction with poisoning with Na^+. Bayerlein et al. [5] studied the effect of framework aluminum removal from, and Na^+ addition to, a commercial USY zeolite. For a series of Na^+-substituted catalysts, activities for isobutane conversion all fell on the same straight line when plotted as a function of $\{[Al] - 3[Na]\}$. The factor of three was obtained by trial and error. The physical interpretation of these results is that the addition of one Na^+ ion is equivalent to the removal of three Al^+ framework ions (a similar approach was used to quantify the relationship between the addition of K^+ ions and the removal of Al^+ framework ions).

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In this work, we quantitatively re-analyze our data [1] on the conversion of cumene as a function of Na^+ level and coke level, now using the approach of [5]. In order to provide the basis for discussion, we first briefly describe the apparatus, materials and experimental procedure used by us, as well as the general model used in our laboratory to describe and quantify the coking process.

2. Experimental details

The three zeolites considered here are of type Y and were supplied to us by W.R. Grace. NaO percentages and other physical properties of the materials are provided in Table 1. In moving from Zeolite 1 to Zeolite 3, i.e., from 48 Na^+ ions per unit cell to 28 Na^+ ions per unit cell, we are probably removing only ions in the so-called Type-II sites, those outside the hexagonal faces of the supercage [6]. A fourth zeolite, with 12 Na^+ ions per unit cell, is not considered here. Its behavior was noted earlier to be qualitatively different from the other three, perhaps due to the fact that, in moving from 28 to 12 Na^+ ions per unit cell, we are probably removing ions in the Type-II′ sites (inside the hexagonal face of the sodalite) and the Type-I′ sites (inside the sodalite, near the hexagonal prism).

The pulse-flow microreactor is a modified Cahn System 113 thermogravimetric analysis (TGA) unit. The apparatus, described earlier [1], allows operation of the TGA unit at ambient pressure, yet allows transfer of products and reactants at high pressure to the on-line gas chromatograph (GC), a Varian 3300 with a flame-ionization detector (FID). Approximately 5 mg of catalyst is heated at reaction temperature (500°C) for 3 h and accurately weighed. Pulses of cumene of size 5 μl are injected into a flowing stream of helium. The outlet stream leaving the catalyst flows through a sample collector at liquid-nitrogen temperature, where condensibles are captured. After a reproducible amount of time from the injection of the pulse, the sample collector is isolated, and the contents heated until they return to the vapor phase. Thereafter, they are flushed into the GC with high-pressure helium. The activity of the catalyst during that pulse can then be obtained from the GC, and the incremental coke level is obtained from the TGA. Thus we have an unambiguous measure of activity as a function of catalyst deactivation.

Table 1
Physical properties of NaHY zeolites used (Si/Al=5.0; unit cell size=24.65 Å)

Sample No.	1	2	3
% Na_2O	11.8	10.5	7.3
No. of Na^+/unit cell	48	42	28
% N	<0.01	<0.01	0.02
Surface area (m^2/g)	947	985	914
TPD activity (μmol/g)	1130	1102	1876
NH_3 activity (μmol/g)	473	544	946

3. Coking model

Curves of coke deposition as a function of time on stream (or of the total amount of reactant) are prevalently of a sigmoidal shape. Further, when the coke deposition curves assume other shapes, those can frequently be considered as special cases of the sigmoidal shape, with one of the features exaggerated. These observations have led us to consider an autocatalytic (or initiation–propagation) mechanism for coke deposition, and we have used such a model extensively. In this model [7], coke entities may be deposited on an uncoked portion of a catalytic surface (the non-catalytic or initiation part); however, the presence of the coke increases the rate of coke deposition on the surface adjacent to the coke (the catalytic or propagation part). The incremental coke deposition $\mathrm{d}C$ corresponding to an incremental addition of reactant $\mathrm{d}R$ can be written as

$$\mathrm{d}C = \{k_1(C_M - C) + k_2 C(C_M - C)\}\mathrm{d}R, \tag{1}$$

where k_1 and k_2 are the rate constants for initiation and propagation respectively, and C_M corresponds to complete coverage of all sites. Integrating this relation leads to

$$C = \frac{C_M\{1 - \exp[-k_1(1 + IC_M)R]\}}{IC_M \exp[-k_1(1 + IC_M)R] + 1}, \tag{2}$$

a relation of the amount of coke deposited C as a function of the total amount of reactant R (suitable for a pulse reactor). Alternatively, the relation can be written as

$$C = \frac{C_M\{1 - \exp[-k_1(1 + IC_M)Vt]\}}{IC_M\exp[-k_1(1 + IC_M)Vt] + 1} \qquad (3)$$

for coke level as a function of the time-on-stream t (suitable for a continuous reactor). Here I represents the ratio k_2/k_1, and V is the molar flow rate of reactant.

Eq. (2) and Eq. (3) have been used [7] to fit coking data from our laboratory and other laboratories, using pulse and flow reactors over a variety of conditions. As expected, C_M is a function of only the catalyst type and pretreatment, while the coking rate constants, k_2 in particular, depend upon the reactor type. In a flow reactor, the value of k_2 is relatively small, whereas it increases with increasing time between pulses, but levels off for time intervals greater than 5 min. The implication is that coking studies should be carried out in a reactor similar to that in which the actual reaction will be proceeding. In this regard, a pulse reactor may be regarded as close to the riser reactor actually used for cracking (or, at any rate, closer that a continuous-flow reactor).

The balance between initiation and propagation leads to an inflexion point in the coke deposition curve, or a maximum in the rate of coke deposition. We term this rate as the Maximum Incremental Coke Deposition (MICD), and the corresponding coke level is termed C_{MI}. C_{MI} is related to the balance between uncoked sites (where coke can deposit) and coked sites (where additional coke formation can be auto-catalyzed). The coke levels C_{MI} and C_M are two important parameters in describing coking and in analyzing activity and selectivity. As noted earlier [1], the coke formed at levels between C_{MI} and C_M is more likely to be multi-layered, while the coke formed between 0 (fresh catalyst) and C_{MI} is more likely to be monolayered. In [1], we presented, for the three catalysts of Table 1, data on the activity and selectivity to various products as a function of coke level and Na^+ level. These data show that activity and selectivity patterns qualitatively change with Na^+ level and C_{MI}.

4. Results and discussion

Fig. 1 shows the conversion over the three zeolites in terms of the coke level and the Na^+ level, for coke levels less than C_{MI}. To combine the deactivating effects of Na^+ and coke, we look for expressions of the type:

$$f([\text{Coke}], [Na^+]) = [\text{Coke}] + n \cdot [Na^+]. \qquad (4)$$

The deactivation functions in the x axis of Figs. 1–3 are therefore of the type shown in Eq. (4). Values of the index n of Eq. (4) used in Figs. 1–3 are 1, 9, and 16, respectively. For convenience, the units of [Coke] and $[Na^+]$ are each weight percent of the catalyst.

Also shown in each of the figures is the best-fit straight line drawn through all of the data points. The best fit is deemed to be the line which minimizes the norm, N, where

$$N = \{\Sigma(X_{\text{exp}} - X_{\text{fit}})^2\}^{1/2}. \qquad (5)$$

In Eq. (5), the summation is over all data points, X is the conversion, and subscripts "exp" and "fit" refer to the experimental and fitted (line) values, respectively. From the figures, it is clear that the points in Fig. 2 cluster closest to the line, relative to Figs. 1 and 3. As might be expected, the value of the norm N is lower when the index n is equal to 9 than for n=1 or n=16.

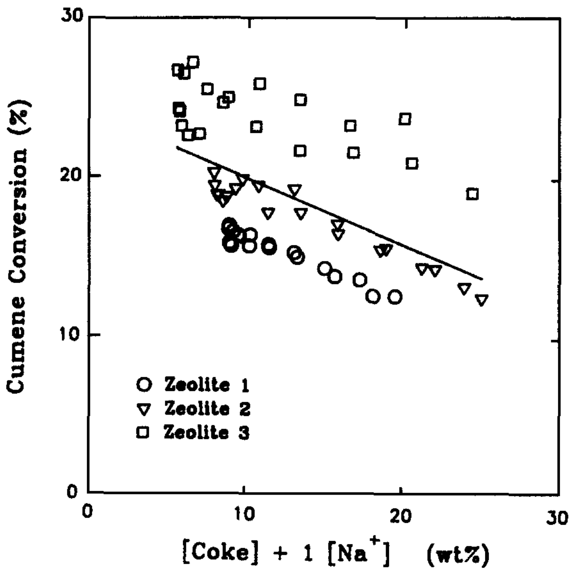

Fig. 1. Conversion for cumene cracking over a series of NaHY zeolites deactivated by coke. The Na^+ content of each catalyst is shown in Table 1. Experimental data from Ref. [1]. The form of the x axis allows the conversion to be plotted against the deactivation function of Eq. (4) with n=1. The line represents the best-fit straight line through all the points.

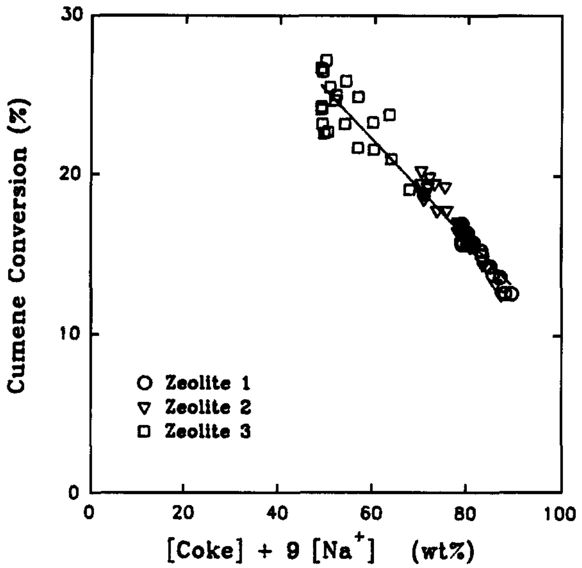

Fig. 2. Conversion for cumene cracking over a series of NaHY zeolites, each with different Na^+ content, each deactivated by coke. Experimental data from Ref. [1]. For the deactivation function, Eq. (4), the parameter n is set equal to 9. The line represents the best-fit straight line through all the points.

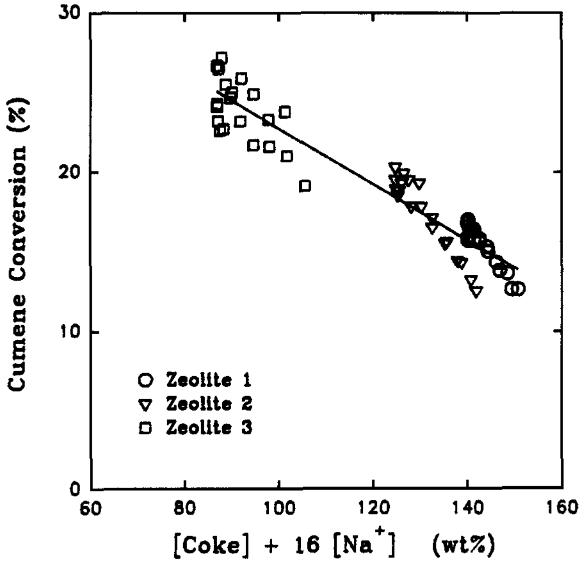

Fig. 3. Same as Fig. 2, except that n is set equal to 16.

Values of the index n were altered from 1 to 20, and for each resulting curve a value of the norm N was calculated. In Fig. 4 is plotted the norm N as a function of the index n. The lower the value of the norm, the closer lie all the experimental data to the straight line. It can be seen that the norm drops rapidly as n increases, upto $n \approx 9$, passes through a minimum, then increases gradually with increasing n, finally appearing to level off at values of n greater than 20. Hence the conversion–deactivation data can best be fitted to a single line when the conversion is plotted as a function of $\{[\text{Coke}] + R\,[Na^+]\}$, where R lies between 8.5 and 9.5. Note that Fig. 2 illustrates the "best" best fit when R is set equal to 9, the whole number in the middle of the range given above.

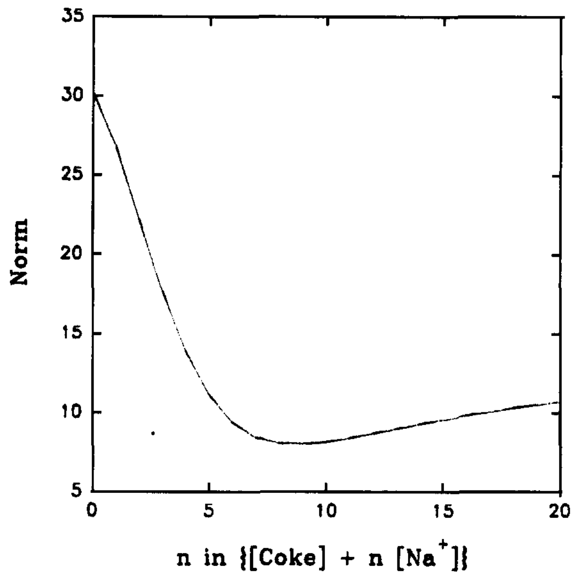

Fig. 4. Norm N as a function of the deactivation parameter n. Note the minimum at $n \approx 9$.

Of course, there is no reason to restrict the conversion–deactivation relationship to a straight line, as in Figs. 1–3. However, results from our laboratory [1,8] do show a straight-line relationship for a given Na^+ level, at least for coke values upto C_{MI}. Even so, examination of the data indicates that replacing the straight line with a curve would lead to no significant changes in the results. That is to say, R, the single "best" value of n, would not be significantly changed.

Accordingly, in terms of deactivation, 1 wt% of Na^+ is equivalent to R (≈ 9) wt% of coke, at least in the range of $[Na^+]$ and [Coke] used here.

Proceeding further, we note that the structure of coke is ambiguous but it can be written as a combination of CH_x moieties, i.e., $(CH_x)_y$. Then $1/A_{Na}$ moles of

Na^+ are equivalent to $R/(y\{A_C+A_Hx\})$ "moles" of coke, where A_i denotes the atomic weight of species i. From the work of Bayerlein et al. [5], one Na^+ ion may be considered equivalent to approximately three Al^+ ions. Hence, it is reasonable to expect that one Na^+ ion poisons S acid sites of the zeolite, where S lies between 2.5 and 3.5. Then y, the number of CH_x moieties deactivating one acid site of the zeolite, can be obtained from:

$$S(1/A_{Na}) = R/(y\{A_C + A_Hx\}). \tag{6}$$

The value of x varies from coke to coke but is of the order of magnitude of unity. This leads to the following value of y

$$y = 23R/(13S). \tag{7}$$

When upper and lower bounds of R and S are substituted in Eq. (7), the value of y obtained is

$$y = 5.5 \pm 1.2. \tag{8}$$

Eq. (8) suggests that the coke moiety adsorbing on a single active site consists of a portion of a condensed aromatic. Specifically, the coke can be thought of as a combination of some single-ring aromatics adsorbed on a single active site (corresponding to y=6) and some condensed two-ring aromatics adsorbed on two active sites (corresponding to y=5) and perhaps even some condensed three-ring aromatics adsorbing on three active sites (corresponding to y=4.7). This is consistent with the physical picture of the initiation–propagation model of coking. Initially, one aromatic would be adsorbed, and this would favor the adsorption of other coke moieties adjacent to it.

It should be noted that the data leading to Eq. (8) were obtained for coke levels of less than C_{MI}. As noted above, we expect that coke deposits will be predominantly monolayered in this region. For coke levels greater than C_{MI}, multilayer coke may be expected. Hence the number of CH_x moities associated with an acid site can be expected to increase. In other words, the value of y is expected to increase if this analysis were carried out in the region between C_{MI} and C_M.

Finally, it is worth mentioning that this analysis yields primarily the relationship between coke deposition and poison deposition, in the form of $R \approx 9$. However, the analysis also yields information on the structure of the coke deposits, in the form of $y \approx 5.5$, and this is done without benefit of surface analytical techniques. Presumably such techniques could be used for confirmation.

5. Summary and conclusions

A quantitative analysis has been established, whereby the roles of coke and poison can be compared, at least at relatively low coke levels. In this manner, we can analyze two coupled deactivation effects. In the range used here, for cumene cracking over a NaHY zeolite, the sodium ion has nine times the deactivating effect of coke, on a weight basis. The method also allows the coke deposited to be characterized, without the use of quantitative surface analytical techniques. Under the present conditions, there are, on the average, between 5 and 6 CH_x moieties of coke that deactivate an active acid site. This is consistent with the model of coking kinetics used.

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