The Role of Zeolite Pore Structure During Deactivation by Coking

Residues accumulating within the cavities of a small-pore zeolite, isolated by extraction, are composed of a series of aromatics up to a distinct cutoff at pyrene. Similar analysis of partially-regenerated catalyst reveal pathways by which residue oxidation can occur and pathways by which these residues can participate during methanol decomposition.

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SCOPE

During the 1970s in the United States, concern over dependence on foreign oil resulted in heightened activity in the investigation of alternative hydrocarbon sources. Due to the potential availability of methanol from coal, the catalytic conversion of methanol into fuels and chemical feedstocks appeared to provide an attractive route for utilizing this country's coal resources.

The use of a small-pore zeolite such as chabazite during methanol decomposition can provide high selectivity toward ethylene and propylene at high rates of conversion per reactor pass; unfortunately, chabazite employed in this reaction quickly deactivates via coking. The objective of this study was to uncover the reaction pathway leading to these coke residues.

The formation of coke was quantified by determining the coke content of spent catalyst samples via weight loss upon combustion. Correlations of coke formation based on this adopted burnoff method provided clues to the origins of coke and to the factors that influence its formation.

Further insight into the molecular nature of coke was provided by analyzing the solvent-extractable portion of residues from spent chabazite samples. Extractions from both the outer surface of catalyst particles and from the internal pore structure (after destroying the crystalline framework by acid treatment) demonstrated the effect that the local microscopic environment can have on the deposition of coke.

The activity of coked catalysts can be regenerated by high-temperature combustion of the carbonaceous residues. Common industrial practice dictates only a partial regeneration wherein a certain acceptable catalytic activity is restored. Characterization of the post-regeneration coke residues by similar extraction experiments has revealed the involvement of coke residues in certain surface reactions as well as some interesting chemistry. These particular findings along with the unique molecular shape-selectivity of zeolites suggest a novel tool for fundamental mechanism studies in areas where low concentrations result in prohibitive analytical problems.

CONCLUSIONS AND SIGNIFICANCE

The formation of carbonaceous residues in the reaction of methanol to hydrocarbons over the small pore zeolite, chabazite, has been followed quantitatively by measuring the coke content of spent catalyst samples. Coke contents, determined by weight loss upon combustion, were in agreement with overall material balances and with analysis of reactor effluent during regeneration cycles. The deposition of coke was found to increase with increasing yields of paraffins and with diminishing yields of olefins. This suggests that the overall formation of coke is by the saturation of some olefins while increasing the degree of unsaturation of other species (coke precursors).

This hypothesis was substantiated by examining the chemical nature of these carbonaceous deposits through gas chromatography-mass spectrometry (GC-MS) analysis of extractable portions. Coke residues on the outer surface of spent catalyst particles were extracted with both CS_2 and CCl_4, while extractions of residues within the zeolitic pore cavities were made after destroying the crystalline framework by acid treatment. The outer surface extract was a diversified mixture in which polynuclear aromatics such as naphthalene, anthracene, and their alkylated derivatives could be positively identified. Besides aromatics the presence of high-molecular-weight saturated hydrocarbons was clearly evident. The differences between the outer surface extract and the intracrystalline extract suggests that there are restrictions on the formation of bulky species due to pore size. The possibility of a difference in the active sites on the crystal surface compared to the sites within the zeolite cages is also suggested.

The abundance of extractable intracrystalline species was four orders of magnitude greater than the concentrations obtained by extracting the outer surface alone. The intracrystalline extract was composed of strictly aromatics ranging from toluene

and xylenes, through the homologous series of polynuclear aromatics up to and including the tetracyclic, pyrene. In contrast to the outer surface extract, this spectrum exhibited a distinct cutoff after pyrene. The molecular dimensions of the smallest of these, toluene, is significantly larger than the limiting aperture of the chabazite channel system while the size of the largest molecule, pyrene, is in excellent agreement with the dimensions of the internal cavities of chabazite. Thus, these products accumulate because of their molecular dimensions within the internal cavities of the crystalline zeolite. Deactivation of the catalyst is thus caused by pore filling and blocking of the active sites.

The trapped intracrystalline residues were characterized after a partial regeneration of the catalyst upon combustion in air. The spectrum of components after such a regeneration was found to be significantly transformed. However, the surviving polynuclear aromatics and the resulting heterocyclic (both oxygenated and nitrogenated) compounds agreed with well established theories regarding resonance stabilization. Furthermore, the soot and smoke formation from fire is known to be comprised of polynuclear aromatics. Thus these results substantiate the findings of others that such molecules as biphenyl, dibenzofuran, and many other heterocyclics are part of the trace chemistry of combustion. Evidence is also presented that suggests benzo[c]cinnoline is formed from the cyclo-addition of molecular nitrogen to biphenyl. A similar reaction is postulated to occur in combustion of diesel fuels.

INTRODUCTION

Chabazite Structure

The structural building blocks of all zeolites are silica and alumina tetrahedra which are linked through the oxygen atoms and can be arranged in various geometric configurations. These various configurations give rise to differing crystalline frameworks which differentiate the many known zeolites.

The internal cavity structure of chabazite has been reported by Barrer (1964) and Dent and Smith (1958). Relatively large internal ellipsoidal cavities or cages were observed. The dimensions of these cavities are approximately 6.7 × 10 Å (0.67 × 1.0 nm) (Breck, 1974). The cavities are linked by windows or apertures creating an infinite network.

The size of these apertures, which provide the only access to the internal cavities, is determined by the number of Si or Al atoms which make up their cross section. In chabazite the cavities are linked by six-ring and eight-ring windows. For adsorption of organic molecules, the channel system of chabazite is restricted to the eight-ring pore openings. The dimension of these pores of somewhat elliptical shape have a major and minor diameter of 4.4 and 3.1 Å (0.44, 0.31 nm) (Smith, 1962).

Reaction of Methanol to Hydrocarbons

Methanol has been converted to low molecular weight olefins (Lin et al. 1978; Anthony and Singh, 1980; Singh et al., 1980; Liu et al., 1984) and to higher molecular weight paraffins and aromatics over a variety of different zeolites (Chang and Silvestri, 1977; Dejaifve et al., 1980). Although the shape-selectivity of each zeolite is different due to differences in their basic pore structure, the fundamental acid catalysis apparently remains the same.

It is well known that methanol and other oxygenated compounds can be selectively transformed into hydrocarbons in the gasoline boiling range (Chang and Silvestri, 1977). In order to increase the selectivity toward low molecular weight olefins, Kaeding and Butter (1980) modified ZSM-5 with trimethyl phosphite. The less active modified catalyst produced low molecular weight olefins in high yields, which could also be formed on the original untreated catalyst by significantly reducing the contact time.

Based on the influence of contact time on the product distribution, Chang and Silvestri (1977) proposed the following sequential reaction path for the conversion of methanol into hydrocarbons:

2 $CH_3OH \rightarrow CH_3OCH_3 \rightarrow C_2$ to C_5 olefins →

paraffins
aromatics
cycloparaffins
C_{6+} olefins

On the small-pore zeolites such as chabazite the principal olefin products are limited to the C_2 through C_4 alkenes, while the final products of the reaction are the corresponding C_2 to C_4 paraffins (Liu et al., 1984). No aromatics or cycloparaffin products are observed since their molecular dimensions are significantly greater than the limiting apertures of the chabazite pore structure. One hypothesis is that these larger products are formed within the internal cages and therefore are restricted from passing through the connecting windows because of their sheer physical size. Once synthesized, such products can only accumulate within the pores of the catalyst, reducing the accessibility of reactant molecules to active sites, and ultimately leading to the deactivation of the catalyst. This hypothesis is substantiated in this work.

The parallel formation of saturated hydrocarbons and aromatics from olefinic species with acid catalysis has been known experimentally for some time (Ipatieff and Pines, 1936). The details of such reactions as illustrated in Figure 1 are now understood in terms of classical carbenium ion chemistry (Jacobs, 1977; Gates et al., 1979).

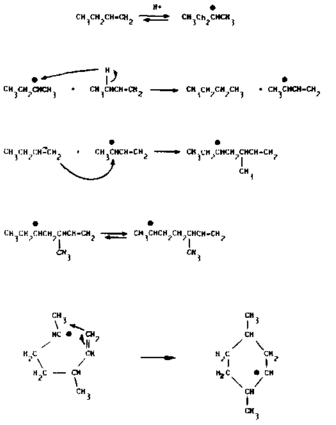

Figure 1. Acid-catalyzed hydrogen and hydride transfer, dimerization, and cyclization reactions leading ultimately to the parallel formation of aromatics (via further dehydrogenations) and alkanes from olefins.

Deactivation of Zeolites via Coking

Venuto and Hamilton (1967) were the first to report the trapping of large molecules within the internal cages of faujasite during the ethylation of benzene. These large-pore zeolites have channel apertures on the order of 10 Å (1.0 nm). A qualitative analysis was given to three fractions obtained by treating the faujasite with HCl and extracting the residue with chloroform. The first fraction consisted largely of highly alkylated benzenes, the second consisted mainly of a series of polyalkyl naphthalenes, and the third fraction was a complex mixture of polyalkyl naphthalenes and alkylated higher condensed polycyclics. No estimate was made of the size of the condensed polycyclics.

The origin of coke deposits in the large-pore zeolites, mordenite and Y, during aromatic alkylation, has been traced with radioactively labeled mixtures (Walsh and Rollmann, 1977). Equal incorporation of aromatics and alkanes into the coke led the investigators to conclude that the alkylation of aromatics is the initial step in coke formation on these zeolites. Similar results were found with ZSM-5 (Walsh and Rollmann, 1979) but with much lower coke yields.

Rollmann (1977) and Rollmann and Walsh (1979) conducted a systematic study of several zeolites with varying pore structures. Intracrystalline coking was proposed to be a shape-selective process directly related to zeolite channel dimensions. A higher selectivity toward coking was observed with erionite than with ferrierite. The difference was attributed to the large internal cavities of erionite.

Langner and Meyer (1980) studied the mechanism of coke formation in the reaction of butadiene over the large pore zelite Y. Toluene extracts of spent catalysts were analyzed by GC-MS, and polynuclear aromatics were identified, but no mention was made of whether the zeolite crystalline framework was destroyed prior to extraction.

The deposition of coke on three zeolites differing by the size and shape of interconnecting channel networks—ZSM-5, offretite, and mordenite—was investigated by Dejaifve et al. (1981) during the reaction of methanol to hydrocarbons. Initial coking rates per Bronsted acidic site were found to be essentially constant on all three zeolites, indicating that initial coking activities are directly related to the availability of Bronsted acidic sites. Subsequent coking and aging rates were found to depend on the pore size and the nature of the channel network. The amount of coke deposited on mordenite or offretite was almost proportional to their respective free pore volumes, while this was not the case for H-ZSM-5. Calculations indicated that the maximum amount of coke formed on H-ZSM-5 corresponds nearly to the deposition of a graphitic monolayer on the external surface.

It becomes apparent that for those zeolites which have frameworks consisting of internal cages with larger dimensions than their corresponding connecting apertures that the possibility of a "reverse" molecular sieving effect is evident. However, if the notion is accepted that these molecules accumulate because they are trapped within a cage, then this cage must physically restrict the dimensions of the largest molecule which can be formed therein.

EXPERIMENTAL PROCEDURES

Catalyst

Chabazite was obtained in a commercial grade, Linde AW-500 molecular sieves, from the Union Carbide Company in $^1/_{16}$ in. (0.16 cm) cylindrical pellets. The fresh catalyst pellets were crushed, ion-exchanged with a solution of NH_4^+ and rare earth chlorides, calcined, and sized to particle diameters ranging from roughly 100 to 400 micron with an average diameter of 173 micron. The preparation of the catalyst is described in detail by Garza (1983) and Liu et al. (1984).

Analyses for the four most prominent rare earths were performed courtesy of Gulf Research and Development Company on the ground chabazite after ion exchange but before use and on the completely regenerated catalyst after repetitive use. The results are:

	La	Nd	Ce	Pr
After ion exchange, before use, wt. %	1.87	0.55	0.37	0.38
After repetitive reactor use, wt. %	1.89	0.52	0.38	0.38

Clearly, there was no reduction in the rare earth content of the catalyst upon repeated use.

Galbraith Laboratories performed aluminum analysis and arrived at a total Al content of 7.33 wt %. Based on these values the ion exchange procedure resulted in a 25% theoretical exchange of NH_4^+ and total rare earths for the calcium ions in the as received zeolite.

Reactor

The details of the fluidized bed reactor employed are given elsewhere (Liu et al., 1984). A novel feature of this laboratory reactor was that catalyst particles could be continuously fed and withdrawn during operation, thereby allowing steady state data to be obtained.

Deactivated catalyst was regenerated via combustion in air in this same reactor with continuous feed and withdrawal of catalyst particles.

Coke Content Determination

Four to six grams of a representative sample of the gray-black spent chabazite were weighed in a dual pan balance with an accuracy of 0.5 mg. This balance had a desiccant placed within its closed boundaries. Whenever possible, transfers of the spent catalyst sample were done in a desiccator with P_2O_5 desiccant in order to minimize the exposure of the highly adsorbent zeolite to the laboratory environment.

Spent catalyst residues were combusted in an electric muffle furnace equipped with a temperature controller. After two hours in the furnace at roughly 840 K the sample was removed and placed in the desiccator for approximately one hour to cool, after which time it returned to its original yellow-tan color. The two-hour burnoff period was established by noting that extended residence beyond two hours at 840 K resulted in no further significant change in weight. The difference in weight before and after the burnoff constituted the assignment of the coke content of the catalyst.

Spent Catalyst Extraction

Chabazite samples with carbonaceous residues which were to undergo extractive analysis with acid treatment (to destroy the crystalline zeolite framework) were first ground with a mortar and pestle. Solvent extractions with no acid treatment (to extract those species on the outside catalyst surface) were also performed, with and without mechanical crushing. Three to five grams of spent catalyst were normally used for the extractions.

Approximately 20 mL of concentrated HCl (8.9 molarity) was added to the catalyst sample with stirring and allowed to stand for six to ten hours. Gas was observed to evolve particularly during stirring, and the acidic mixture slowly took on a greenish-black tint. After standing, an equal volume (20 ml) of distilled water was added to dilute the concentrated acid.

Next, roughly 40 mL of either CS_2 or CCl_4, obtained from Fisher Scientific (Reagent grade, A.C.S.), was added to the greenish-black aqueous phase in a separatory funnel. This funnel was shaken, to promote contact between the now precipitated zeolitic gel and solvent, and allowed to stand for four to eight hours. The once-clear solvent phase took on a golden yellow color. This phase was then separated, washed with distilled water, and centrifuged to remove fine catalyst particulates.

The approximately 30 ml of recovered solvent phase was then concentrated via mild heating under a nitrogen purge to remove excess solvent. One milliliter of a rich amber-colored sample for gas chromatographic analysis was obtained. When no acid treatment was employed the solutions were concentrated to approximately 100 μL in an attempt to magnify any extractable portion from the outer chabazite surface. None of the extracts from experiments without acid dissolution ever changed from the clear color of the pure solvent.

TABLE 1. CORRELATION BETWEEN COKE PRODUCTION AND DEFICIENT ELEMENTAL CARBON BALANCES

	Temperature and Fluidized Bed Run No.								
	703 K					723 K		743 K	
	328	329	330	333	334	331	325	332	326
TWHSV*, h^{-1}	0.4	0.4	2.0	1.8	1.5	1.9	0.4	1.9	0.4
Diluent	---	---	---	N_2	H_2O	---	---	---	---
MeOH Conversion, %	100	98	35	55	41	44	100	49	100
% Closure of Carbon Balance	82.0	90.9	98.9	97.5	99.1	95.9	81.9	95.4	81.0
Catalyst Coke Content, g coke/g coke-free catalyst									
Initial (Feed)	0.046	0.072	0.051	0.074	0.074	0.051	0.042	0.057	0.022
Final (Effluent)	0.072	0.093	0.120	0.107	0.108	0.112	0.079	0.111	0.075
coke deposited/100 g of methanol fed	11.5	7.8	3.6	2.6	4.0	3.2	9.1	3.0	13.1

$$\text{* Total Weight Hour Space Velocity} = \frac{\text{Total mass flow rate of reactant stream}}{\text{Mass of catalyst hold-up within the reactor}}$$

The GC analysis was performed on a Varian 4600 gas chromatograph with a VISTA 401 microprocessor and flame ionization detector. The chromatographic column, 20 ft (6.1 m) in length and 1/8 in (0.32 cm) O.D., was packed with 100–120 mesh size 10% OV-101 (methyl silicone) packing. The injection port and detector temperatures were 573 K and a 0.6 to 1.0 μL sample size was used for injections.

Extracted species were identified via GC-MS utilizing both the packed column described above and a 25 m, bonded phase BP5 (5% phenyl methyl silicone) fused silica capillary column. A Hewlett-Packard model 5980A mass spectrometer with quadrupole mass filter was employed and analysis performed with electron ionization (EI) of 70 eV and scanning m/z range from 45 to 400.

RESULTS AND DISCUSSION

Quantifying Coke Formation

One of the ways in which coke formation on a catalyst manifests itself is through resulting deficient material balances. In fact, this is one means of quantifying coke formation. However, failure to close material balances can also be indicative of leaks in the reactor system or combined experimental errors in analyzing the effluent and feed streams.

Another method to quantify coke formation is to leave the spent catalyst within the reactor after an experiment and completely remove any carbonaceous deposits via combustion by passing air through the reactor at high temperature. Analysis of the effluent during this cycle allows the estimation of the coke content of the catalyst. However, this method requires the complete regeneration or removal of all carbonaceous deposits. For those instances where partial regenerations are desired, such as to study the effect of catalyst coke content on catalyst activity, another method is needed. Thus, the method of estimating coke content via weight loss upon combustion of representative spent catalyst samples was employed. As shown in Table 1, coke contents were in agreement with overall material balances from the methanol reaction. Analysis of reactor effluent during complete regeneration also agreed with the coke content determinations. The effect of reaction temperature and of diluents in the reactant feed stream on the rate of coking is presented. Figure 2 illustrates the relationship between lack of closure of the carbon balances, and the yield of paraffinic species in the product stream. This figure also presents the closure of the total material balance including coke.

Figure 3 illustrates that the deposition of carbonaceous material increased with increasing yields of paraffins and with diminishing yields of olefins. These findings suggest the parallel formation of saturated (paraffin) and further unsaturated species (aromatic coke) from the unsaturated olefins. This is in agreement with classical carbenium ion chemistry via acid catalysis of olefins.

Spent Catalyst Extractions

Solvent extractions of spent catalyst samples were undertaken with a goal of isolating coke precursors. Identification of such in-

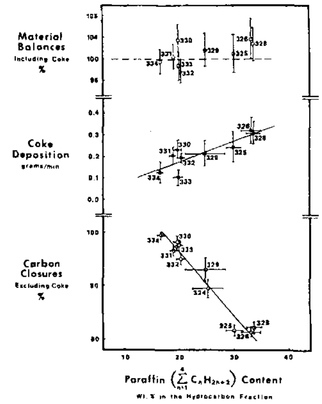

Figure 2. Relationship between deficient material balances and the deposition of carbonaceous residues with their corresponding correlation with the paraffin content in the product mix.

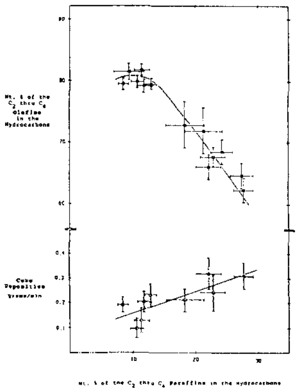

Figure 3. Relationship between enhanced coke formation with increasing yields of paraffins and diminishing yields of olefins.

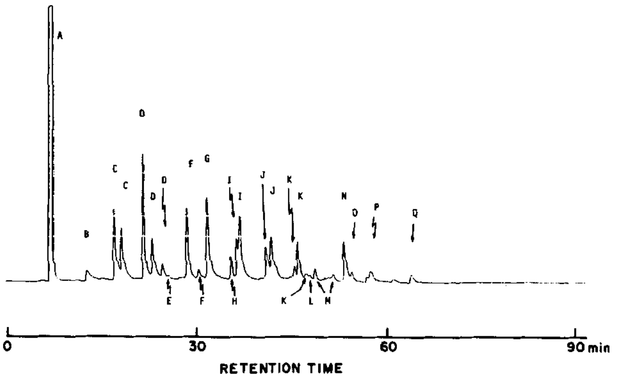

Figure 4. Gas chromatogram of concentrated carbon tetrachloride extract of spent catalyst powder after acid dissolution (spent chabazite sample collected after runs 333 and 334 and which were mixed prior to the 7-23-82 regeneration); Labeled components are identified in Table 2. Chromatograph column was 20 feet of 10% OV-101. Temperature program was 4 K per min from 323 K to 563 K, then isothermal for 30 min.

TABLE 2. GC-MS IDENTIFICATION OF EXTRACTABLE SPECIES LABELLED IN FIGURES 4 AND 5

A	Carbon tetrachloride (Solvent)
B	Toluene
C	Xylenes
D	Various isomers of trimethyl benzene
E	Indene
F	A mixture of C_4 alkyl derivatives of benzene with tetramethyl benzenes as the most likely candidates. Also evidence for small amounts of methyl indane.
G	Naphthalene
H	Various isomers of trimethyl ethyl benzene
I	The two isomers of methyl naphthalene
J	Isomers of dimethyl naphthalene
K	Trimethyl naphthalenes are the most likely candidates although there is some evidence for other C_3 alkyl side chain derivatives as well
L	Diphenyl methanone
M	Tetramethyl naphthalenes are the most likely candidates although small amounts of methyl derivatives of fluorene are suspected.
N	Anthracene or phenanthrene (on the basis of the mass spectral information alone these species were indistinguishable).
O	A mixture of dimethyl C_3 alkyl derivatives of naphthalene.
P	Methyl phenanthrene
Q	Pyrene or fluoranthene (on the basis of mass spectral information alone the species were indistinguishable).

termediates would certainly provide further insight into the mechanism of such reactions. Samples were extracted with CS_2 and CCl_4 with and without treating the samples with acid. The concentrated extract of samples not treated with acid showed only a solvent peak in the gas chromatogram.

The extract of the acid treated samples, as shown in Figure 4 and identified in Table 2, contained numerous extractable species. This is a direct consequence of the crystal structure of chabazite. Its porous framework is known to contain a three-dimensional network of large ellipsoidal cavities connected by smaller apertures. The effective opening of these apertures or "windows" governs the size of the molecules which can enter (and leave) the porous channel system of chabazite. Based on the well accepted experimental fact that acid treatment chemically ruptures the crystalline framework of zeolites such as chabazite (Breck, 1974), the two analyses reported above clearly indicate the following conclusion: Molecules can accumulate within these cavities, presumably trapped there because of their molecular size or shape. These molecules are trapped at least until acid dissolution destroys the restrictive apertures of these cavities. This finding illustrates the "reverse" molecular sieve effect first observed by Venuto and Hamilton (1967).

However, something else is evident from the chromatogram in Figure 4. There is a definite cutoff in the chromatographic peaks after that peak observed at a retention time (RT) of roughly 65.9 min and labeled Q. The presence of such a cutoff should not come as a surprise if the hypothesis is accepted that these molecules accumulate because they are trapped within a cage. The cage would restrict the dimensions of the species which can be formed therein.

Furthermore, Breck (1974) reports the dimensions of the internal ellipsoidal cavities of chabazite as approximately 6.7 × 10 Å (0.67 × 1.0 nm). Based on the benzene carbon-carbon and carbon-hydrogen bond lengths of 1.39 and 1.10 Å (0.139 and 0.110 nm), respectively, the estimated dimensions of the largest extracted component, pyrene, is on the order of 6.7 × 9.2 Å (0.67 × 0.92 nm). Equivalent carbon-carbon bond distances throughout the molecule were assumed, which is not entirely correct in many of the polynuclear aromatics such as pyrene. Thus these dimensions are given as simply rough estimates of the static dimensions between extreme proton nuclei. Furthermore, at the reaction temperature of 703 K, the pyrene molecule would possess substantial vibrational energy. Such a temperature would also alter the chabazite framework through expansion. Hence, the identification of pyrene as the largest trapped intracrystalline molecule is in excellent agreement with the hypothesis that the definitive cutoff in the chromatogram of Figure 4 is due to the dimensional restrictions of the cavity structure on the size of the molecule which can be synthesized therein.

Chang and Silvestri (1977) reported the detailed product spectrum from the conversion of methanol over H-ZSM-5. The free diameter of the pores of this zeolite are on the order of 6 Å (0.6 *nm*) and would therefore allow the elution of aromatic derivatives reported by these authors. Comparison between the aromatic products from H-ZSM-5 and the lower molecular weight intracrystalline residues of chabazite allows the following conclusions. The preponderance of methyl-substituted benzenes illustrates that the fundamental acid-catalyzed chemistry of the solid zeolites is remarkably similar. The shape-selectivity of the individual zeolite is simply a secondary physical restraint on the course of the catalyzed transformation. The abundance of toluene and xylenes over ethylbenzene in the products reported by Chang and Silvestri is due to more than the restrictive pore openings of H-ZSM-5. It is an inherent characteristic of the catalysis of the reaction. This comparison between the aromatic products of H-ZSM-5 and the extracted residues of Table 2 also supports the conclusion that the isolated extracted species were formed within the chabazite cavities during the course of the methanol reaction, and are not a result of any transformation occurring during the acid dissolution or subsequent extract sample workup.

Catalyst samples from a partial regeneration of the spent catalyst were extracted with carbon tetrachloride after acid dissolution. The extract was concentrated to roughly 0.5 mL. This highlighted the appearance of several new peaks. The resulting chromatogram is given in Figure 5 and illustrates even more prominently the lack of peaks after a RT of roughly 65.7 min. Individual molecular species, are listed in Tables 2 and 3.

Although the extract corresponding to Figure 5 was clearly concentrated further than that of Figure 4, a comparison between the two chromatograms can still be made which indicates the following. The major components in the overall spectrum are still

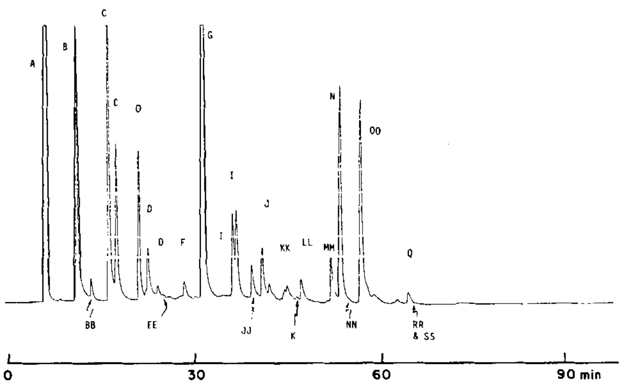

Figure 5. Gas chromatogram of the concentrated carbon tetrachloride extract of spent catalyst powder after acid dissolution (spent chabazite sample collected after the 7-23-82 partial regeneration cycle). GC conditions are as in Figure 4. Labeled components are identified in Tables 2 and 3.

present; however, there are significant changes in their relative abundance along with the appearance of several new peaks. The highly alkylated aromatics, such as the C_4 alkyl derivative (cpd F), trimethyl ethyl benzenes (cpd H), tetramethyl naphthalenes (cpd M), along with the C_3 alkyl dimethyl derivative of naphthalene (cpd 0), appear to be highly susceptible to oxidative degradation. This is evident by the sharp decrease in the relative areas of the peaks at retention times of roughly 31.8, 33.5, 37.0, 51.2, and 56.8 min. Clearly, bond-scission during oxidation occurs initially and much more readily on the alkyl side chain than within the aromatic ring itself. This is further illustrated by the enhanced stabilities of the polynuclear aromatics, napththalene (cpd G) and anthracene (cpd N).

In the chromatogram of Figure 5 there is also the appearance of new peaks at retention times of 42.1, 47.1, 49.5, 53.7 min, and the prominent peak at 58.5 min. These correspond to biphenyl (cpd JJ), dibenzofuran (cpd KK), fluorene (cpd LL), fluoren-9-one (cpd MM), and benzo[c]cinnoline (cpd 00), respectively. Other oxygenated species found in trace amounts were xanthen-9-one (cpd NN), anthracenone (cpd RR), and benz[de]anthracen-7-one (cpd SS). That such a small degree of partial oxidation has occurred on a vast number of species indicates that there is very likely a limiting supply of oxygen during regeneration within the zeolitic channels due to diffusional resistances. These resistances can be extreme in the case of the deactivated catalyst with residues filling the pores. The ability to isolate these partially oxygenated, conjugated systems is also due to their enhanced resonance stability. This is the driving force for the formation of these particular oxygenates.

TABLE 3. GC-MS IDENTIFICATION OF EXTRACTABLE SPECIES IN FIGURE 5 NOT OBSERVED IN FIGURE 4

BB	Perchloroethylene (impurity in the solvent)
EE	Indane
JJ	Biphenyl
KK	Dibenzofuran
LL	Fluorene
MM	Fluoren-9-one
NN	Xanthen-9-one
OO	Benzo[c]cinnoline
RR	Anthracenone
SS	Benz[de]anthracen-7-one

The last two oxygenated compounds were at very low levels although positive identification was made.

Since the only oxygenated species found in the spent catalyst after a reaction experiment (see Figure 4 and Table 2) was diphenyl methanone (cpd L) and only in trace amounts, the partial oxidation during regeneration is apparently reversible. The oxygenated aromatics must undergo hydrogenation during the course of a methanol reaction when significant hydride and hydrogen transfers are taking place. Thus, the oxygenated components of a partially regenerated catalyst take an active part in the resulting surface reactions.

The isolation of oxygenated conjugated aromatics such as dibenzofuran during combustion of catalytic deactivating residues parallels the recent hypothesis that such molecules are part of the trace chemistry of fire (Bumb et al., 1980). When chlorine was present as a trace component of the hydrocarbon fuel, Bumb et al (1980) reported finding chlorinated dibenzo-p-dioxins, chlorinated dibenzofuran, and chlorinated biphenyls during combustion. Since soot and smoke from fires is known to be comprised of polynuclear aromatics similar to the residues isolated in the deactivated chabazite, the present findings support the hypothesis that such large oxygenated hydrocarbon molecules can be formed during combustion. Evidence that these highly conjugated oxygenates can be formed from the partial oxidation of polycyclic aromatic precursors is also presented.

Further evidence that the coke residues left after a partial regeneration take an active part in the catalytic surface reactions is the finding of an abundance of biphenyl after such a regeneration cycle. Its formation possibly results from the combination of two phenyl radicals after oxidative degradation of their corresponding side chains. Another possible origin is by oxidative degradation of the highly susceptible carbon atoms at the 9 and 10 position in phenanthrene. However, no appreciable quantity of biphenyl was observed after the catalyst had been involved in the course of a methanol reaction. Apparently, biphenyl is transformed, such as by ethylene alkylation of the two adjacent rings, into the highly stable polynuclear aromatic, phenanthrene.

Along similar lines as the cycloaddition of ethylene to biphenyl to form phenanthrene is the possible addition of molecular nitrogen to biphenyl to form benzo[c]cinnoline. The formation of nitrogen oxides during combustion with air is well known, thus the lability of the nitrogen-nitrogen triple bond during such high temperature processes is not entirely new. However, the formation of such a large, specific heterocyclic as benzo[c]cinnoline in significant quantities (compare the relative area of this peak in Figure 5) is best explained by the following. The nitrogen molecule retains a double bond along with incorporation into a highly resonance stabilized, polycyclic aromatic system. This is a large driving force for any reaction, even one which transforms molecular nitrogen. The fact that there were no other nitrogenated compounds further supports such a conclusion.

Yergey et al. (1982) characterized organic adsorbates on diesel particulate matter by a combination of chromatographic and mass spectrometric techniques. Besides an abundance of polynuclear aromatics, the nitrogenated compounds benzo[c]cinnoline and nitropyrene were reported. Nitropyrene was found in only trace amounts while benzo[c]cinnoline was reported in relatively high concentrations. However, biphenyl was also reported in appreciable quantities. Thus, the conclusions made above regarding the formation of benzo[c]cinoline from the cycloaddition of molecular nitrogen to biphenyl provides insight into the origins of this compound on diesel particulates, as well.

Further evidence that component (or components) eluting at a retention time of 65.8 min represents the physical extreme of the trapped intracrystalline components and, in fact, does come from the internal cavities is provided as follows. Another extraction with no acid treatment was performed, but this time the 30 mL of extract was concentrated to roughly 100 μL, i.e, four orders of magnitude more concentrated than the previous extractions. The

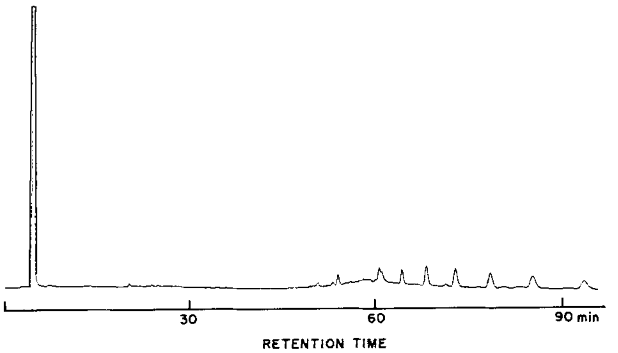

Figure 6. Gas chromatogram of highly concentrated carbon tetrachloride extract of spent catalyst pellets (spent chabazite sample collected after the 7-23-82 partial regeneration cycle). GC conditions are as in Figure 4.

resulting chromatogram for the spent catalyst powder (grinding of the pellets) is given in Figure 6. The presence of the peaks at retention times of 65.7 (pyrene), 55.4 (anthracene), 53.2 (tetramethyl naphthalenes), and 25.1 (trimethyl benzenes) min indicate that these species are also formed on the outer zeolite surface as well as within the intracrystalline cavities. However, there are also prominent peaks beyond that at 65.7 min. Since the size of the peaks at longer retention times than pyrene are approximately equal to pyrene, then one would expect to see them in the chromatogram of Figures 4 and 5. They are not, and thus pyrene (or the isomeric fluoranthene) eluting as the final peak in Figures 4 and 5 must have been extracted from the intracrystalline cavities.

The comparison between the outer surface extract and that obtained from within the internal cavities is facilitated in Figure 7. This is a different catalyst sample than is illustrated in Figures 5 and 6. Thus, not only were the results for a given lot of samples highly reproducible, but the replication of the spectrum of components obtained between lots should be noted (compare, for instance, Figures 5 and 7b).

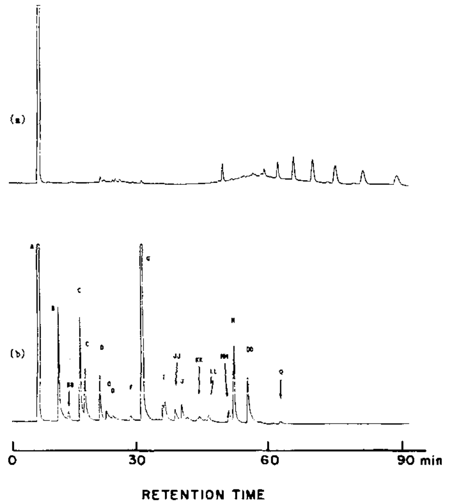

Figure 7. Gas chromatograms of (a) highly concentrated extracted of spent catalyst pellets, and (b) the concentrated carbon tetrachloride extract of spent catalyst powder after acid dissolution (spent chabazite sample collected after the 7-12-82 partial regeneration cycle). GC conditions are as in Figure 4. Labeled components are identified in Tables 2 and 3.

Identification by GC-MS of individual molecular species in the outer surface extract was greatly hampered by the poor resolution of the complex mixture. Nonetheless, polynuclear aromatics such as naphthalene, anthracene, and their alkylated derivatives were positively identified. Besides aromatic moieties the presence of high moleculecular weight alkyl groups was also evident. It appears that bulky side chains can form on the outer surface, but their formation within the internal zeolitic channels is ruled out because of the physical restrictions of the framework.

ACKNOWLEDGMENT

The financial support of Texaco, Inc. and Dow Chemical U.S.A. for this project: of the AMOCO Foundation for fellowship support of K. McLaughlin; of the Texas Engineering Experiment Station; and of the Department of Chemical Engineering, Texas A&M University is greatly appreciated.

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Manuscript received Feb. 14, 1984; revision received Oct. 29, 1984, and accepted Oct. 29.