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Coke Formation in Zeolite ZSM-5

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The coke contents and sorption capacities of three ZSM-5 zeolites with different Al/Si ratios were followed during methanol conversion until the zeolites were completely deactivated. For two of the zeolites the volume of coke exceeded the concomitant decrease in void volume, so that some coke must have been sited on the external surfaces of the zeolite crystals. An estimate was made of the ratio of external to internal coke for these zeolites. For the third zeolite the assumption that there was some external coke implies that there was also some topological blocking of parts of the channel system by coke. The presence of internal coke in the third zeolite was deduced by selective removal of coke by oxidation in an oxygen plasma and was confirmed by X-ray diffraction.

INTRODUCTION

The zeolite ZSM-5 has become a major commercial catalyst, finding application in a number of industrial processes. One of these, the so-called MTG process (*1*), is based on the ability of ZSM-5 to convert methanol to gasoline for extended periods (*2*). However, ZSM-5 does eventually deactivate due to the buildup of carbonaceous residues generically termed coke which block access of reactant molecules to the catalytic sites and which must be removed by combustion in oxygen in order to regenerate the catalyst. The low rate of deactivation of ZSM-5 has been attributed (*3–7*) to the dimensions of the pores which sterically hinder the formation of coke-producing intermediates (i.e., shape selectivity) and to the relatively low density of acid sites.

Reported coke contents on ZSM-5 after methanol conversion range from 2 to 60% (*6, 8–10*), the highest value being from the Mobil pilot plant (*10*). These experiments were of course carried out on different ZSM-5 catalysts and, as we will show here, the rate of formation and amount of coke produced can vary considerably between different catalysts. Another major variable which could account for these differences is the time scale of the experiment. Most laboratory experiments have not explored the behavior of ZSM-5 at extended reaction times and have only measured the amount of coke formed after relatively small and varying amounts of methanol or dimethyl ether (DME) have been converted. Our results show that coke continues to form long after the cessation of liquid hydrocarbon production or the breakthrough of DME. Presumably, in the pilot plant experiments the catalyst at the top of the reactor bed would have been exposed to large amounts of methanol after deactivation. The effects on coke formation of pelletization and the presence of the binder are also unknown.

The site of coke formation has not previously been considered in any detail. It has been stated (*8*) that during methanol conversion coke forms on the external surfaces of the ZSM-5 zeolite crystals and it has also been suggested (*9*) that "a type of paraffinic coke" forms within the channels. Langner (*6*) suggested that coke formed on ZSM-5 was aromatic and formed both externally and within the pores.

In this work we have studied three ZSM-5 zeolites, measuring their sorption capacity for nitrogen and correlating this with the amount of coke formed at various stages during the conversion of methanol to liquid

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and gaseous hydrocarbons. These measurements show an inverse relationship between the accessible internal volume of the zeolite crystals and the volume of the coke. Together with X-ray diffraction data and the selective removal of coke in an oxygen plasma, these methods have enabled us to investigate the site of the coke, whether internal or external, and to correlate this with the total amount of methanol converted before the zeolite was deactivated.

EXPERIMENTAL

The three different ZSM-5 zeolites (Nos. 1, 2, and 3) were prepared with different Al/Si ratios according to published methods (*11*, *12*). Before use they were converted to the acid form via repeated ammonium ion exchange following the techniques described by Jacobs and von Ballmoos (*13*). Aluminum and silicon analyses of the three catalysts were obtained by conventional means and are given in Table 1. The sodium contents of the three H-ZSM-5 zeolites were found to be less than 1% of that found in the Na form.

Examination by SEM and XRD did not reveal any minor phases or the presence of amorphous material. The observed crystal morphologies are also described in Table 1.

Coking experiments were carried out at 1 atm pressure in an all-glass reactor. The catalyst was supported on a 35-mm-diameter glass frit and the bed was made shallow (ca. 2 mm in depth) to try to produce uniform coking of the zeolite. The bed was also well mixed at intervals short compared to the sampling period. The first 1 g of methanol per gram of ZSM-5 (i.e., 1 g g^{-1}) was injected through a septum into a stream of nitrogen in 0.05-ml increments. The bed was well mixed after each injection and the first sample of zeolite was taken after a total of 0.5 g g^{-1} had been injected. A methanol and nitrogen mixture was then introduced in a 1 : 1 ratio (by volume at 370°C) with a methanol feed rate of 0.8 g h^{-1}. The amount of catalyst at the beginning of the experiment was ca. 0.8 g which, after removal of the samples required for coke and sorption capacity determinations, was reduced to ca. 0.4 g by the end of the experiment. This gave an initial methanol weight hourly space velocity of ca. 1 g g^{-1} h^{-1}, rising to ca. 2 g g^{-1} h^{-1} at the end of experiment.

TABLE 1

Characteristics of Zeolite ZSM-5 Samples and Coking Results

	ZSM-5		
	No. 1	No. 2	No. 3
Aluminum content (%)	1.31	0.62	1.17
Si/Al	35	74	39
Particle size (μm)	0.5	0.5–2	2 to 4
Morphology	Cubes	Cubes	Spheres[a]
Precursor void volume fraction	0.005	0.005	0.002
H-Form void volume fraction	0.303	0.290	0.273
Void volume fraction at complete deactivation	0.046	0.084	0.045
Coke content when liquid hydrocarbon production ceased (%)	17.0	18.4	14.1
Maximum coke content (%)	26.7	23.2	16.5
Initial rate of coke formation[b]	1.6	0.83	12
Overall rate of coke formation[b,c]	0.64	0.36	0.45

[a] Polycrystalline spheroids, individual crystals ca. 0.1 μm.

[b] Units are (grams of coke per Al site per gram of methanol carbon converted) × 10^{23}.

[c] Defined in text.

Before the bed was mixed or a sample of zeolite removed, the methanol flow was stopped and the catalyst held at 370°C for 10 min in the nitrogen flow, to ensure removal of volatiles. The reactor was then allowed to cool to room temperature under nitrogen. Samples of ca. 10 to 15 mg were taken and equilibrated at 21°C over saturated K_2CrO_4 at a relative humidity (RH) of 88% (*14*) for a minimum of 2 days. Before the reactor temperature was raised to its normal operating value, care was taken to ensure the absence of oxygen by flushing the reactor with nitrogen.

ZSM-5 catalysts readily sorb a few percent of air and water vapor after removal from the reactor. Since the results given here are expressed in terms of the coke- and air-free zeolite, it was essential that the composition of the ZSM-5 remain unchanged between the determinations of coke content and sorption capacity. Equilibration at 88% RH produced a ZSM-5 with a composition which did not vary noticeably when exposed to the laboratory environment.

Sorption capacity measurements were made using a dynamic BET method (*15*). In order to remove air and water from the ZSM-5 the H-form and coked zeolite samples were outgassed in a nitrogen/helium gas stream for at least 1 h at 350°C (i.e., 20°C below the methanol reaction temperature) before the sorption capacity was measured. The ZSM-5 had Type 1 adsorption isotherms (*15*) and all sorption capacities were determined using a nitrogen/helium gas mixture ($P/P_0 = 0.25$). In order to ensure no loss of occluded organics the sorption capacities of the ZSM-5 precursors were determined after outgassing at room temperature only. The sorption data obtained at 21°C were adjusted to STP, and void fractions were calculated from the volume of nitrogen absorbed, assuming a liquid nitrogen molar volume of 29.5 cm^3 (*16*).

The coke content of the zeolite samples were determined by combustion in a thermobalance. The samples were heated to 350°C at 10°C per minute in a flow of 30 cm^3 helium per minute, and held at that temperature until no further weight loss occurred. A side stream of 10 cm^3 of oxygen per minute was then introduced and the temperature was raised to 700°C at 10°C per minute. The weight loss between room temperature and 350°C was attributed to the desorption of air and water, and that between 350 and 700°C to the combustion of coke (Fig. 1). Both the sorption capacity and the coke content are expressed in terms of the mass of zeolite at 700°C which corresponds closely to framework atom and counterion mass only.

The weight percentage coke contents were converted to volume relationships assuming a ZSM-5 density of 1.79 g cm^{-3} (*16*) and a coke density of 1.22 g cm^{-3}. These values were obtained in a series of separate experiments, in which it was found that the C/H ratio of the coke formed on ZSM-5 No. 3 increased with the coke content, from ca. 0.8 at very low coke contents to ca. 2 at very high coke contents. It was not possible to distinguish if this change in C/H ratio was due to a change in the molecular composition of existing coke or if different forms of coke were deposited at different stages of deactivation. Similar changes have also been observed (*7, 17*) in the C/H ratios of coke formed on zeolites. The increasing C/H ratio is likely to result in an increase in the density of the coke. The value of ca. 1.22 g cm^{-3}, obtained from Ref. (*18*), assumes that the coke was polyaromatic with a composition similar to coal and an average C/H ratio of 1.25. A density of ca. 1.39 g cm^{-3} corresponds (*18*) to a C/H ratio of 2. The effect of this increasing C/H ratio will be to reduce the apparent rate of increase in the volume of coke as the amount of coke increases. However, as this change is relatively small it is unlikely to affect the arguments used here.

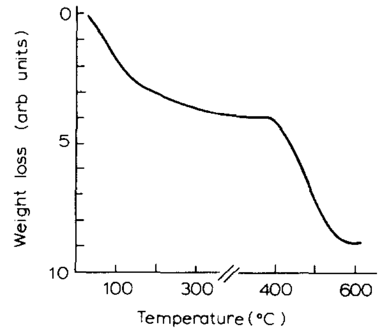

FIG. 1. Thermogravimetric curve typical of coke-containing ZSM-5 zeolites. the temperature was held at 350°C until the weight became constant. Oxygen was then introduced and the heating recommenced.

It was not practicable to analyze the liquid hydrocarbon product which was collected in a room temperature trap. However, the point at which production of liquid hydrocarbons ceased was noted. The qualitative composition of the gaseous products was determined using an off-line gas chromatograph.

In an attempt to selectively remove any external coke, samples of completely deactivated zeolite No. 3 were exposed for varying times to an oxygen plasma (*19*) in a

RF field derived from a modified medical diathermy generator. The oxygen radicals generated in a plasma are highly reactive and will readily combine with reduced carbon species to form CO and CO_2. However, if the surface is essentially inert (i.e., SiO_2) then there will be a high probability that the radicals will recombine to form dioxygen and desorb. At low RF power levels (ca. 5 to 10 W) the sample temperature remains close to ambient, thus avoiding thermal oxidation. The action of an oxygen plasma is, in principle, to remove coke from external surfaces only; thus powdered samples must be disturbed at intervals to expose fresh material. In this work ca. 10-mg samples were spread in a thin layer some 10 mm below the plasma region in a vertical glass test tube which formed part of the plasma ashing system, and disturbed frequently to expose fresh surfaces of the zeolite crystals. Coke and sorption capacity measurements were made on samples exposed for increasing times under the same conditions of RF power and oxygen pressure.

Powder X-ray diffraction patterns of these samples were obtained after equilibration at 88% RH.

RESULTS AND DISCUSSION

The appearance and physical characteristics of the zeolite powders changed as the coke content increased. Initially white, they became distinctly gray after only a small amount of methanol (ca. 1 g g^{-1}) had been passed, and black after ca. 10 g g^{-1}. At low coke levels the zeolite powder tended to agglomerate and adhere to the walls of the reactor, while at higher coke levels the powder became free-flowing. This change in behavior coincided with the cessation of liquid hydrocarbon production and the presumed absence of "sticky" high boiling residues on the external surfaces of the zeolites. Alternatively there may have been a change in the nature of the coke, for example to a graphitic form.

Figure 2 shows the coke content versus the amount of methanol passed through the reactor. The arrows in Fig. 2 indicate the cessation of liquid hydrocarbon production, and give an indication of the relative

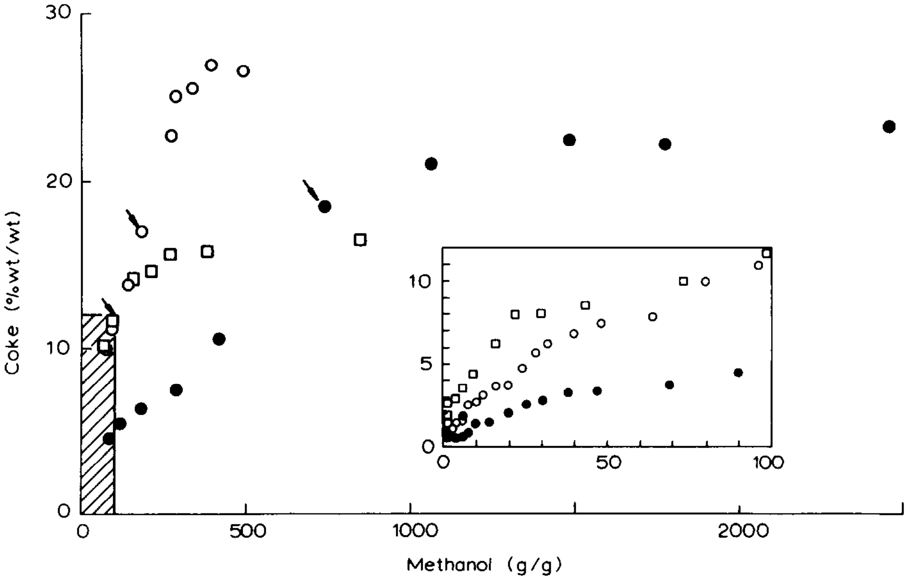

FIG. 2. Coke content versus methanol passed through the ZSM-5 catalyst bed. ZSM-5 No. 1 = ○, No. 2 = ●, and No. 3 = □. The data from the hatched area are shown with an expanded methanol scale in the inset box. The arrows indicate the cessation of liquid hydrocarbon production.

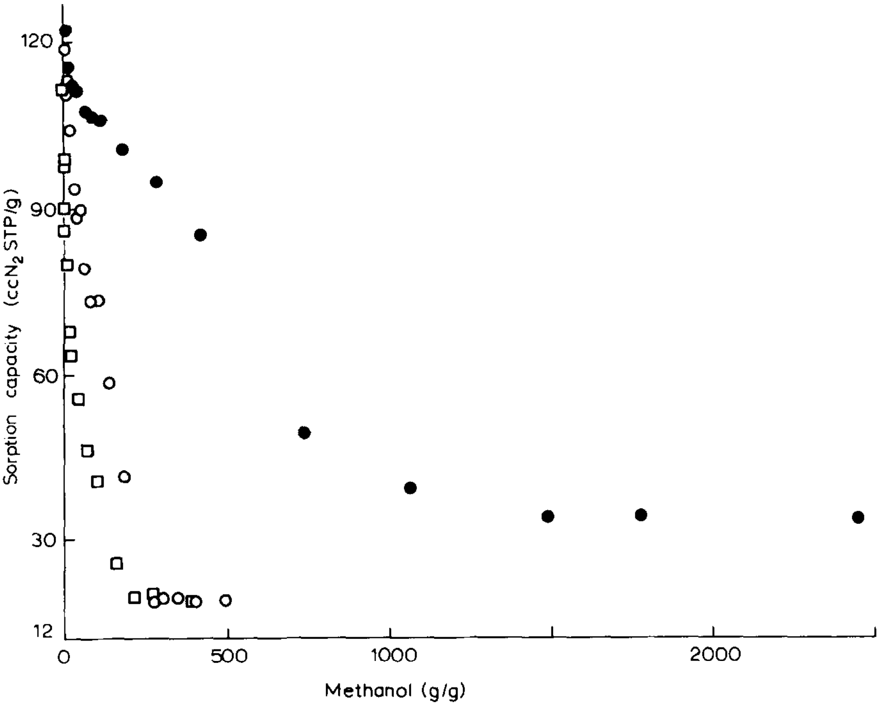

FIG. 3. Sorption capacity for nitrogen versus methanol passed through the ZSM-5 catalyst. ZSM-5 No. 1 = ○, No. 2 = ●, and No. 3 = □.

abilities of the three zeolites for methanol conversion. DME breakthrough occurred at about the same time as liquid hydrocarbon production ceased, and methanol breakthrough occurred soon after. However, gaseous hydrocarbon production continued after DME breakthrough. The composition of the hydrocarbons changed from one containing C2 to C4 hydrocarbons to one which was almost pure ethane. DME production continued for some time after gaseous hydrocarbon products were no longer detectable although it eventually ceased and only methanol could be detected. This point at which DME production ceased was taken as the point of complete deactivation. Although it is not obvious from Fig. 2, coke formation never ceased even after complete deactivation. This slow, but continual, coke buildup was probably due to thermal cracking of the methanol on the hot catalyst bed, and may account, in part, for the high levels of coke formed in the pilot plant operation (*10*).

All three zeolites showed a relatively high initial rate of coke formation (inset to Fig. 2). The initial rate of conversion of the carbon in methanol to coke was determined by extrapolation to zero, assuming that coke is pure carbon. The overall rates of coke formation were defined as the slope of each curve when 50% of the final coke level had been reached. Table 1 shows the initial and overall rates, the saturation level of coke, and the coke content at which liquid hydrocarbon production ceased, for each zeolite. The overall rate of coke formation is seen to be related to the aluminum content of the ZSM-5, which confirms the findings of Ione *et al.* (*20*), but the initial rate of coke formation and the ultimate amount of coke formed were not related either to the aluminum content or to the amount of methanol converted.

Figure 3 shows the sorption capacity for nitrogen versus the volume of methanol passed, for the three zeolites. As seen in Table 1 the sorption capacity of the H-

ZSM-5 was considerably larger than that of the precursor which corresponded to a surface area of ca. 6 m^2 g^{-1} in two of the zeolites and to a surface area of ca. 2 m^2 g^{-1} in the third. We attribute this to sorption only on the external surfaces of the zeolite crystals. The rate of fall in sorption capacity mirrored to a certain extent the rate of formation of coke; for instance, ZSM-5 No. 3, which had the lowest overall performance in conversion of methanol, showed both the most rapid fall in sorption capacity (Fig. 3) and the most rapid rate of coke formation (Fig. 2). The decrease in sorption capacity ceased at the point of complete deactivation and the sorption capacity then remained constant despite further coke formation. The final value obtained for the sorption capacity was substantially higher than the value found for the precursor (Table 1), where we can assume that there was no access to the internal channel structure. We suggest that this "high" value indicates that portions of individual crystals, or possibly even complete zeolite crystals, remained coke free, presumably due to an absence of catalytic sites. The aluminum distribution within "large" crystals of ZSM-5 has been found to vary substantially (*21, 22*) and considerable differences between crystals have been found (*23*). The results obtained here can also be interpreted to suggest that a significant proportion of the ZSM-5 was aluminum free and that the consequent absence of catalytic sites precluded the reactions leading to coke formation. This also implies that some coke formation is intimately associated with the catalytic site. The higher value for the final sorption capacity of ZSM-5 No. 2 may reflect a greater degree of aluminum inhomogeneity than in ZSM-5 Nos. 1 and 3.

Figure 4 shows the sorption capacity as a function of the coke content, with dual scales converted these two measurements into void volume and coke volume relationships. At the beginning of each experiment there was a short time when the effect of coke on the sorption capacity appeared to be relatively variable, particularly for ZSM-5 Nos. 1 and 2 (Fig. 4). However, after conversion of a few grams per grams of methanol there was an almost linear decrease of sorption capacity with coke content. This decrease in sorption capacity ended abruptly after which the sorption capacity remained virtually constant despite a continued coke buildup (Fig. 4).

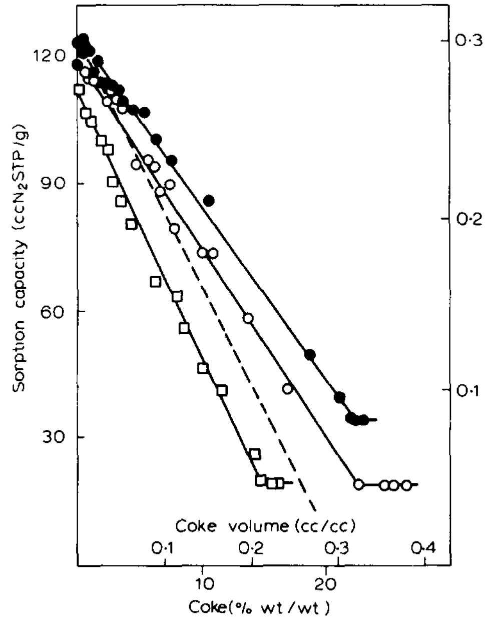

FIG. 4. Sorption capacity and void volume fraction versus coke content and coke volume fraction. ZSM-5 No. 1 = ○, No. 2 = ●, and No. 3 = □. The dashed line is for $S = -C + 0.30$.

The initial void volume fractions (Table 1) of ZSM-5 Nos. 1 and 2 were close to the value of 0.304 calculated (*16*) for the ZSM-5 structure. However, the initial void volume fraction of ZSM-5 No. 3 was significantly lower, which suggests the presence of an impurity phase or occluded inorganic matter (e.g., unreacted gel) in the ZSM-5 channels. As seen in Fig. 4, ZSM-5 No. 3 was also the zeolite for which the void volume decreased most rapidly with coke formation. As a result of the relatively rapid coke buildup and reduction in void volume ZSM-5 No. 3 converted the smallest amount of methanol to hydrocarbons before loss of catalytic activity.

The major portion of each curve in Fig. 4 can be described by a straight line. The equations of these lines are

ZSM-5 No. 1: $S = -0.76C + 0.29,$ (1)

ZSM-5 No. 2: $S = -0.69C + 0.30,$ (2)

and

ZSM-5 No. 3: $S = -1.07C + 0.27,$ (3)

where C is the calculated volume fraction of coke and S is the accessible internal void volume fraction as determined from sorption capacity measurements. Figure 4 also shows the straight line

$$S = -C + 0.30,$$

or

$$S + C = \text{initial void volume fraction}, \quad (4)$$

which describes the ideal situation in which coke C would remove only its own internal volume from the zeolite. Figure 5 illustrates an interpretation of these results in terms of the more general equation

$$S + kC = V_0 \quad (5)$$

where V_0 is the initial internal void volume fraction, ignoring the small contribution from the external surfaces of the ZSM-5 crystals (Table 1).

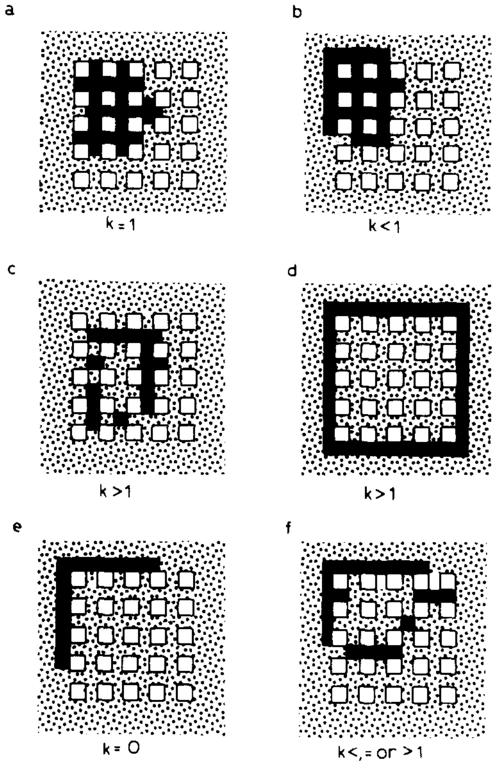

FIG. 5. Schematic representation of possible coke distribution in a zeolite channel system. The space between the squares represents the channels in the zeolite, and the shaded area represents coke.

A number of possible distributions of coke are shown schematically in Fig. 5, together with their effects on the coefficient k in Eq. (5). In the initial state no coke is present and the sorption capacity $S = V_0$. Figure 5a shows the simplest case in which coke fills the zeolite channels in a regular fashion and the volume of coke is equal to the loss in sorption capacity, i.e., $k = 1$. When some coke is external and the channels are filled in a regular fashion by the remaining coke (Fig. 5b), then the total volume of coke exceeds the loss in sorption capacity and hence $k < 1$. In the case shown in Fig. 5c the internal coke is arranged so as to isolate topologically part of the interior of the zeolite, so that a small volume of coke can have a large effect on the sorption capacity, i.e., $k > 1$. Where all the coke is external two different possibilities are as shown in Figs. 5d and e. In the first case the external coke blocks all pore mouths and the sorption capacity is effectively reduced to zero. In the case shown in Fig. 5d, $k > 1$; in principle the thickness of the external coke layer can increase until $k = 1$ and then until $k > 1$. In Fig. 5e the external coke is arranged in such a way as to have no effect on the sorption capacity, and $k = 0$. In the last case, Fig. 5f, both external and internal coke act together to topologically block off or isolate regions of the ZSM-5 channel system. Here different topologies and different ratios of internal to external coke can have a considerable effect on the factor k. Where external coke predominates, then $k < 1$; where internal coke predominates, then $k > 1$. Clearly the situation can arise fortuitously where k is effectively unity. Although a number of other cases can be visualized we feel that these are sufficient for our arguments here.

Since the coefficients of k are less than unity for ZSM-5 Nos. 1 and 2, the volume occupied by the coke must (for the major portion of the deactivation process at least) have been greater than the loss in void volume associated with that amount of coke. This is clear evidence that a significant amount of coke was formed on the external surfaces of these ZSM-5 zeolite crystals. If the situation shown in Fig. 5b is relevant then inspection of Eqs. (1) and (2) shows that the minimum ratios between external and internal coke would be 0.32 : 1 and 0.45 : 1 for ZSM-5 Nos. 1 and 2, respectively. Any topological blocking would increase these ratios.

In the case of zeolite No. 3, k was equal to unity within the experimental error. This means that there was either no external coke at all and consequently no blocking (Fig. 5a) or else there was some external coke, some internal coke, and some topological blocking, the effects combining fortuitously to produce $k = 1$. We have studied this zeolite in more detail below.

The nature of the external coke has not yet been determined. If it were present in a form which had a high surface area, e.g., filamentary coke, then it could provide an alternative explanation for the relatively high sorption capacity of the completely deactivated ZSM-5. However, inspection of completely deactivated ZSM-5 at 100,000 times magnification (a resolution of <10 nm) using STEM did not reveal any structures not seen in the uncoked material. Also, the final surface area did not change significantly despite continued coke formation. We therefore consider it unlikely that large amounts of, for example, filamentary coke were present in the deactivated ZSM-5, and we suggest instead that the external coke was compact in nature. In that the ZSM-5 zeolite with the greater proportion of external coke (No. 2) converted more methanol before deactivation, it appears that external coke is less effective than internal coke in deactivating the zeolite.

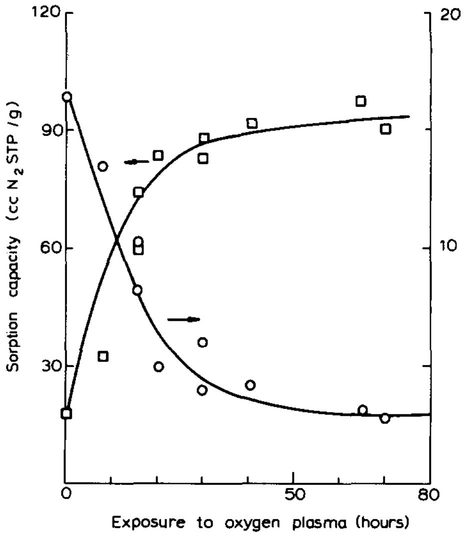

FIG. 6. Sorption capacity and coke content of coke-containing ZSM-5 No. 3 versus time of exposure to an oxygen plasma.

Figure 6 shows the results of the exposure of the fully deactivated ZSM-5 No. 3 to an oxygen plasma at room temperature. As oxidation proceeded the appearance of the zeolite changed from black to gray. However, under the optical microscope some crystals showed varying shades from almost white to dark gray, but most were either black or white.

As Fig. 6 shows, the coke became increasingly difficult to remove, and there appeared to be a low level of coke (ca. 3%) which was resistant to oxidation even at extended exposure times. If we assume that the oxygen plasma predominantly reacts with surface material then the remanent value of 3% coke and the maximum total value of 16.6% coke (Fig. 6) give 4.9 : 1 as an upper limit of the ratio between the external coke and internal coke at maximum deactivation. Taken together with the value of k obtained above, this is then evidence for topological blocking in this zeolite, as shown schematically in Fig. 5f.

A similar, but less detailed, experiment was carried out with sample 2. Here it was found that the coke content reduced from 23 to 1.6%. From the values of k (see above) sample 2 must contain more external coke than sample 3 and the results obtained from the exposure to an oxygen plasma support this. The ratio of external to internal coke in sample 2 has an upper limit of 14.2, cf. 4.9 for sample 3.

While the external surface area of sample 2 is 2.5 times that of sample 3 we are hesitant to draw any simple relationship at this stage between external surface area and external coke content. It is quite possible that more detailed investigations of the surface chemistry of ZSM-5 may reveal characteristics which may relate more closely to the amount of external coke formed.

Further evidence that these ZSM-5 zeolites contained internal coke is given by XRD patterns. It has been shown (*24, 25*) that ZSM-5 undergoes a displacive transformation from monoclinic to orthorhombic when it occludes bulky ions or sorbs organic molecules. The effect of this transformation is to alter the relative peak positions and intensities in the XRD patterns. The most intense peaks in the XRD pattern for samples of ZSM-5 No. 3 are shown in Fig. 7. As the coke content increased, the indicated peak positions shifted from those found in the H form to those typical of the precursor containing occluded TPA ions. By analogy, therefore, we conclude that a proportion of the coke which formed during methanol conversion must be inside the channel system.

On removal of the coke by combustion the original XRD pattern is regenerated, i.e., the ZSM-5 reverts back to the monoclinic form.

CONCLUSIONS

During methanol conversion to hydrocarbons, the amount of coke and its rate of formation were found to vary considerably between the three ZSM-5 zeolites, with up to 26% coke being formed on one of them. Coke formation continued, albeit slowly, even after the production of liquid hydrocarbons and DME had ceased, at the later stages probably due to the thermal cracking of methanol. The overall rate of coke formation was related to the aluminum content of the ZSM-5 but the initial rate of coke formation and the ultimate amount of coke formed were not obviously related to the aluminum content or to the amount of methanol converted (Table 1). The final value for the sorption capacity was substantially higher than the value for the precursor (Table 1) which suggests that a significant proportion of the zeolite was aluminum free, and that (internal) coke formation is intimately associated with the catalytic sites.

A linear relationship was found to describe most of the variation of sorption capacity (expressed as void volume) with

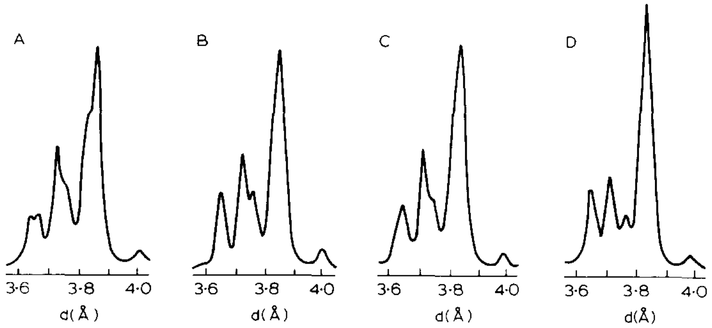

FIG. 7. X-Ray diffraction patterns of ZSM-5 No. 3: (A) H form, (B) precursor form containing tetrapropylammonium ions, (C) H form containing 0.85% coke, (D) H form containing 23% coke.

coke (expressed as a volume fraction of the zeolite volume). Equation (5) was applied to this linear region and showed that the volume of coke exceeded the reduction in void volume in two of the three zeolites, confirming the existence of external coke. In the case of the third zeolite two interpretations are possible: either there was no external coke, with no topological blocking of the interior of the crystals by coke, or both these features were present. In a further study of the third zeolite, a RF oxygen plasma was used to remove coke progressively, presumably from the surface of the crystals. Despite extended exposure times, about 20% of the initial coke was found to be resistant to oxidation. We suggest that this oxidation-resistant coke was inside the zeolite channels and thus protected from the oxygen radicals. XRD patterns showed that coke caused the same lattice structural changes as did the occlusion of large organic molecules or bulky ions, indicating the presence of internal coke. Since gaseous hydrocarbons and DME continue to be formed after liquid hydrocarbon production ceases, internal coke probably forms on the strongest acid sites first and then on progressively weaker sites.

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