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Sorption Studies of Coke Deposited on ZSM-5

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Samples of ZSM-5 catalysts which had been used for converting methanol to hydrocarbons in a test reactor were examined by sorption measurements. Trimethylamine was used to assess the available pore volume and total number of acid sites. Ethyldiisopropylamine, which is too large to penetrate the zeolite channels, gave independent information about the exterior surfaces. The distribution of coke deposits was further probed by sorption kinetic measurements with benzene. In the initial stages of coking, some empty regions of the crystals were sealed off, but thereafter most of the decreased sorption capacity resulted from simple pore filling. Rather little coke was deposited externally. Acid sites were not removed very preferentially, either inside the crystals or on the external surfaces. Exterior coke provided some new, weakly acid, sorption sites, as well as removing the original strong acidity.

INTRODUCTION

This paper describes some gas phase adsorption measurements which were carried out to investigate the deactivation of H–ZSM-5 catalysts which had been used to convert methanol to hydrocarbons in a test reactor.

Equilibrium amine uptakes at 298 K and high relative pressures were used to find the sorption capacity at saturation, while experiments at much lower pressures at 423 K were used to determine the amount of very strong adsorption due to the presence of acid sites.

Trimethylamine (TMA) was used to monitor the total sorption capacity of the catalyst and the total number of acid sites. Ethyldiisopropylamine (EDA), which is too large to penetrate the zeolites pore system, was used to examine the external surface of the crystals.

Measurement of the rate of uptake and loss of benzene gave complementary information which allowed the position of the coke deposits in the catalysts to be probed in more detail.

METHOD

Materials

The zeolite was prepared, converted to the acid form, and pretreated as described previously (*1*). The silicon/aluminum ratio was 37. Electron microscopy showed the sample to consist of polycrystalline lumps, 2–4 μm in diameter which appeared to be composed at 0.1- to 0.2-μm crystallites. No other solid phases were observed.

Gas chromatographic analysis confirmed that the benzene, TMA, and EDA had impurity levels of less than 0.1%. They were degassed by repeated freeze, pump, thaw cycles before use.

Experimental Procedures

The test flow reactor and procedures under which the coked catalysts were produced have been described previously (*1*). The zeolite was present in the reactor as a thin layer of powder, supported on a porous glass frit. Methanol entrained in nitrogen was passed over the catalyst at 640 K. Products were condensed in a liquid nitrogen trap and analyzed from time to time.

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Used catalyst was removed after chosen periods on stream for further investigation. Some details of the samples used in this work are given in Table 1.

Adsorption equilibrium measurements were carried out in a glass volumetric apparatus, equipped with a quartz spiral pressure gauge and Teflon stopcocks (*2*). Adsorption of TMA was rapid at both 298 and 423 K. There was no evidence to suggest that localized sorption of TMA molecules in the channels was blocking access to the zeolite. The initial sorption of EDA was essentially complete by the time that a first pressure reading could be taken (less than 5 min) but thereafter a very slow decrease of pressure with time was observed. Blank experiments showed that the amine uptake was negligible in the absence of zeolite samples.

Adsorption rate measurements were performed gravimetrically at 298 K using a CI Electronics Microforce type 3B electrobalance. The adsorbate pressure was maintained constant at the saturated vapor pressure at 273.2 K by use of a cold finger immersed in a stirred ice bath.

Desorption was carried out by pumping away the gas phase from a previously equilibrated sample.

The catalysts were outgassed at 690 K while pumping under vacuum for 2 h before use. While this has proved sufficient to give reproducible adsorption measurements with most sorbates, including EDA (*3*), this was not the case when TMA was used. Consequently, measurements were always carried out with samples which had not previously been exposed to this adsorbate.

TABLE 1

Catalyst Data

Sample	Time on stream (h)	wt% coke[a]	Products
1	Unused		
2	8	0.86	Hydrocarbons
3	40	3.0	Hydrocarbons
4	170	9.6	Dimethyl ether
5	Extended	23.6	None

[a] Weight of carbon by microanalysis.

RESULTS

Part of the TMA which could be taken up by the solid was very strongly bound. The amount involved was measured by performing sorption isotherm measurements at 423 K (Fig. 1). The total adsorption capacity at saturation was determined for the same adsorbate by experiments at 298 K (Fig. 2). The maximum uptake observed, 8.6 molecules/u.c. on the unused catalyst, corresponded to about 0.14 cm^3 of liquid per gram of zeolite.

Molecular size calculations suggested that EDA should not penetrate the pore system of ZSM-5, and this was confirmed experimentally in the adsorption experiments at 298 K, which showed that there was a rapid, but much smaller uptake of gas than had been observed with TMA (Fig. 3). Experiments at 423 K were complicated by a slow, but continuing sorption. This was probably due to the migration of protons

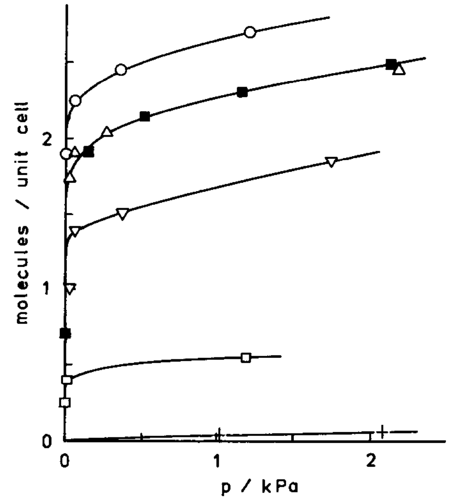

FIG. 1. Trimethylamine adsorption at 423 K. (○) Sample 1, unused; (■) sample 4, after calcination at 820 K in air; (△) sample 2, 0.86% carbon; (▽) sample 3, 3.0% carbon; (□) sample 4, 9.6% carbon; (+) sample 5, 23.6% carbon.

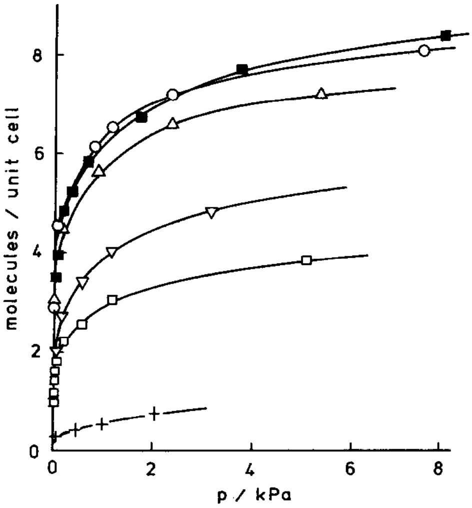

FIG. 2. Trimethylamine adsorption at 298 K. (○) Sample 1, unused; (■) sample 4, after calcination at 820 K in air; (△) sample 2, 0.86% carbon; (▽) sample 3, 3.0% carbon; (□) sample 4, 9.6% carbon; (+) sample 5, 23.6% carbon.

from the zeolite interior at this temperature (*3*). The observed drift rate was about 5 × 10^{-4} molecules/u.c. per minute (*3*). No attempt was made to determine the maximum extent of this slow process, as the experimental error of such an estimate would have been very large. Figure 4 shows data which have been obtained by extrapolation to zero contact time to remove the effect of this slow drift. The experimental results do not allow us to exclude the possibility that a slow reaction of the EDA was occurring, but we have not observed a similar drift with other amines (*3*).

The kinetic experiments with benzene are summarized in Fig. 5, where M_t/M_∞ is the fractional uptake. Only uptake is shown, as the desorption experiments gave a rather similar set of curves. A kinetic study of water adsorption did not show any significantly different features and therefore is not presented here.

DISCUSSION

The saturation capacity of ZSM-5 for TMA when expressed as a volume of liquid per gram of zeolite was only about 73% of the void volume calculated from the crystal structure (*4*). However, this difference probably results from packing restrictions in the limited pore space, as dipropylamine was found to occupy 92% of the void volume in the same sample of zeolite (*3*), and variations of at least this magnitude are common with different adsorbates (*5, 6*). TMA was therefore taken to be a reasonable molecule with which to measure the free pore space in the catalysts, as well as the number of acid sites.

Figure 6 shows that the sorption capacity for TMA at 298 K decreased almost linearly with the carbon content of the used catalyst after an initial more rapid fall.

There are two ways in which we would certainly expect the sorption capacity to be decreased: (i) by simple filling of the pore space by immobilized deposits (hereafter simply called coke) and (ii) by coke sealing off parts of the crystal which then become inaccessible, or blocked. In the latter mechanism, the details of how the sorption capacity declines with coking must depend on

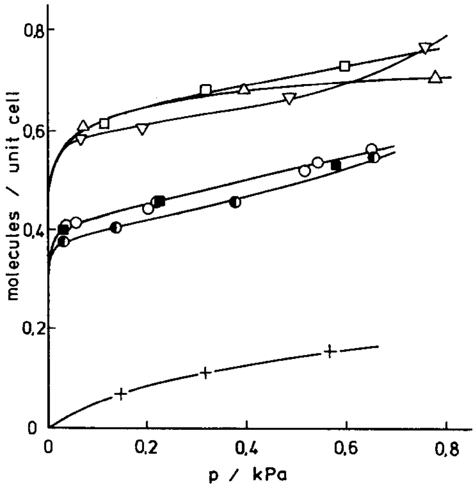

FIG. 3. Ethyldiisopropylamine adsorption at 298 K. (○) Sample 1, unused; (◐) repeat experiment on sample 1, after outgassing at 790 K; (■) sample 4, after calcination at 820 K in air; (△) sample 2, 0.86% carbon; (▽) sample 3, 3.0% carbon; (□) sample 4, 9.6% carbon; (+) sample 5, 23.6% carbon.

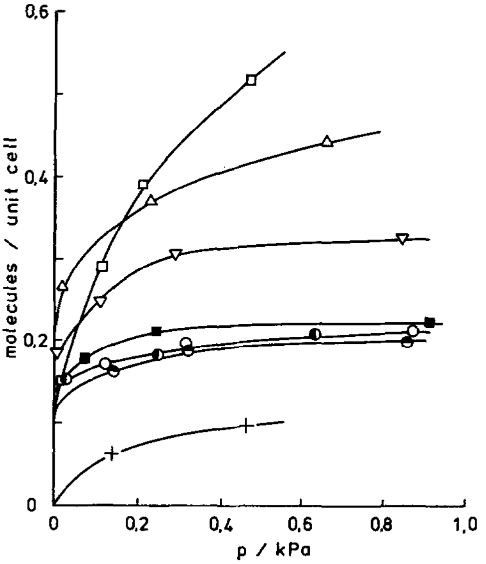

FIG. 4. Ethyldiisopropylamine adsorption at 423 K. (○) Sample 1, unused; (◐) sample 1, unused after extra calcination in air at 820 K; (◒) repeat experiment on sample 1, after outgassing at 790 K; (■) sample 4, after calcination at 820 K in air; (△) sample 2, 0.86% carbon; (▽) sample 3, 3.0% carbon; (□) sample 4, 9.6% carbon; (+) sample 5, 23.6% carbon.

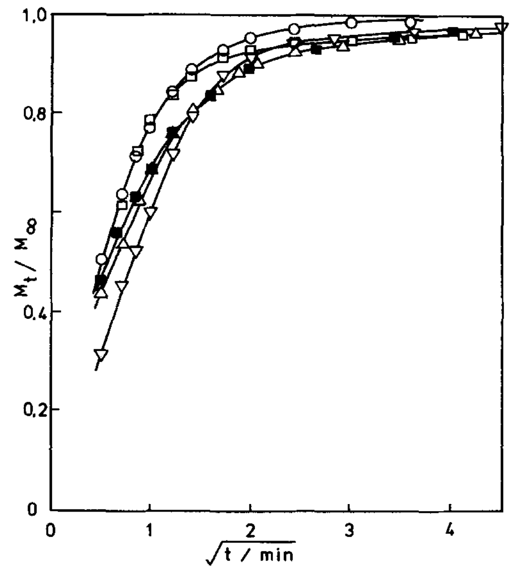

FIG. 5. Rates of benzene uptake at 298 K. (○) Sample 1, unused; (■) sample 4, after calcination at 820 K in air; (△) sample 2, 0.86% carbon; (▽) sample 3, 3.0% carbon; (□) sample 4, 9.6% carbon.

where the coke is deposited, but some general points can be made.

Inevitably, blocking must result in the sorption capacity decreasing more quickly than the volume of deposit alone could account for. However, if the coke is randomly laid down, the effect would initially be very small. This is because in an interconnected pore system, such as that in ZSM-5, few regions become completely sealed off until the amount of deposit is substantial, after which there is a rapid increase in exlcuded volume (*7*). In this case, therefore, a graph of sorption capacity versus carbon content should initially be linear, with a slope which can in principle be calculated from the volume of the carbon deposit. At later stages, the slope must become steeper quite rapidly.

If the coke is preferentially deposited in the outer regions of the crystal or on its surface, we would expect an initial slope equal to or slightly less than that of the above case, but a much more abrupt onset of an appreciable blocking effect. Sorption capacity should become very small, corresponding to sorption only on the external surfaces, well before the pore system is completely filled.

The space filling capacity of the coke deposit can be crudely calculated as explained

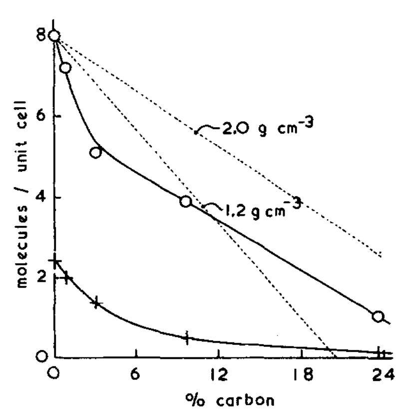

FIG. 6. Trimethylamine sorption as a function of coke content. (○) Approaching saturation at 5 kPa and 298 K; (+) strong sorption at 423 K. The dotted lines represent the pore filling capacity of cokes with densities of 2.0 and 1.2 g cm^{-3}.

before (*1*). The two dotted lines on Fig. 6 correspond to assumed coke densities of 1.2 and 2.0 g cm^{-3} which may reasonably be thought of as minimum and maximum likely values. It is apparent that whichever density is used, the coke initially reduces the sorption capacity for TMA much more rapidly than can be accounted for by simple pore filling. The trend at higher coke levels agrees surprisingly well with the simple model, if the coke density is quite high.

The size and shape of the TMA molecules and the space limitations within the pore system restrict the strong adsorption to one molecule per acid site (*3*). This view is supported by the similarity between the extent of strong adsorption on the uncoked catalyst and the analytical result for the Al content of the zeolite found in this work. The relationship between acidity, adsorption, and Al content is well established (*8*).

Table 2 and Fig. 6 show that the acid site concentration goes down in almost direct proportion to the total sorption capacity, until heavy coke deposits build up. It is interesting that the acid sites are not preferentially removed during the initial stages of coking according to these results. This contrasts with the conclusions derived from previous work which used nitrogen sorption to estimate total sorption capacity (*1*) and ammonia to measure residual acid sites (*9*). It is suggested that the reason for this difference is that even though nitrogen has a greater collision diameter than ammonia, it can penetrate into regions of the partially coked catalyst which are inaccessible to ammonia because of its linear shape. If this is so, the present results give a better estimate of the fraction of acid sites which are removed. Different access of ammonia and pyridine to acid sites has already been reported (*9, 10, 11*).

EDA cannot penetrate the pore system and so can be used to study the exterior of the catalyst crystals. Figure 7 relates the adsorption data to the carbon content of the solids. All the used catalysts, apart from the very heavily coked sample, showed a maximum sorption of about 0.10 mol kg^{-1}. This is a surprisingly high value. It does not seem possible to account for this as an effect of capillary condensation because of the low relative pressures at which the adsorption occurs, the isotherm shape, and the absence of a similar uptake by heavily coked samples. If an area of 0.52 nm^2 is assigned to each adsorbed molecule (calculated from the liquid density) it indicates a surface area of about 30 m^2 g^{-1}. This would imply an average particle diameter of about 40 nm for an adsorbent with density 1.8 g

TABLE 2

Sorption Properties of the Catalyst Samples

Sample	TMA sorption[a]			EDA sorption[a]		
	Total to fill[b]	Strong[c]	Strong/total	Total to fill[d]	Strong[e]	Strong/total
1	8.0	2.4	0.30	0.44	0.15	0.34
2	7.2	2.0	0.28	0.65	0.26	0.40
3	5.1	1.4	0.27	0.62	0.20	0.32
4	3.9	0.5	0.13	0.65	0.14	0.22
5	1.0	<0.1	<0.1	0.08	0.02	0.2

[a] As molecules per unit cell.

[b] Estimated at 5 kPa and 298 K.

[c] At 0.2 kPa and 423 K.

[d] Estimated at 0.2 kPa and 298 K.

[e] At 0.01 kPa and 423 K.

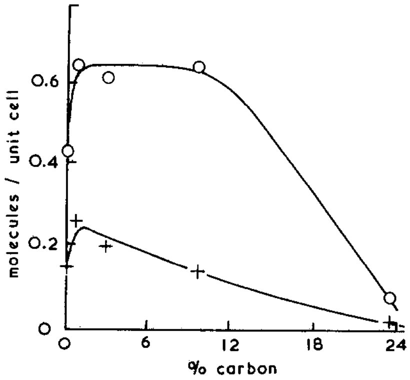

FIG. 7. Ethyldiisopropylamine sorption as a function of coke content. (O) Approaching saturation at 0.2 kPa and 298 K; (+) strong sorption at 423 K.

cm^{-3}. The unused catalyst sorbed about 30% less. The calculated particle size is much smaller than electron microscopy would suggest, but could mean that the smallest particles observed are aggregates or even smaller crystals, or that the outer parts of the crystal are very defective and allow entry of material considerably larger than the window diameter of the zeolite. A similar discrepancy between the expected and the observed amount of adsorption of nonpenetrant molecules has been observed in solution phase adsorption experiments (*12*). A heavily coked sample with 23.6% carbon, which may have been sufficient to saturate a defective surface layer, showed a much smaller uptake, which was approximately consistent with the apparent particle size.

Sorption at 423 K again showed that part of the sorbate was strongly bound. The ratio of strongly sorbed material to adsorption capacity for EDA on the unused catalyst was similar to that observed with TMA, indicating that the readily accessible external and internal surfaces are rather similar. However, as coking proceeded, Fig. 4 shows that the number of strong sorption sites for EDA was increased, though saturation is not achieved at such low pressures as it is on the original surface. Clearly, the coke first laid down can interact quite strongly with the amine and may act as a catalyst in its own right, with somewhat different properties.

Figure 5 shows the kinetics of benzene sorption. Detailed interpretation of curves like these is never possible without a considerable body of information about the particle sizes and shapes in the sample being studied (*13*). However, in this work, each catalyst is derived from one batch of zeolite crystals, so that these geometric parameters should be common to each sample. The similarity of the curves strongly suggests that neither the diffusion coefficient describing benzene migration nor the effective path length which molecules must traverse to fill the crystals change appreciably as the coke deposit builds up. Clearly, only some distributions of coke can be consistent with this, so kinetic experiments can provide information which is complementary to that which can be obtained from equilibrium sorption measurements.

The slow rates observed here do cast some doubt on the assumption that diffusion into the zeolite particles was rate controlling (*14*). However, reducing the sample mass from 100 to 10 mg did not appreciably change the results. We also note that uptake of EDA was even more rapid than that of benzene, which argues against diffusion between zeolite crystallites being the rate determining process.

The rest of the discussion is concerned with the location of the coke deposits. Figure 8 attempts to represent schematically

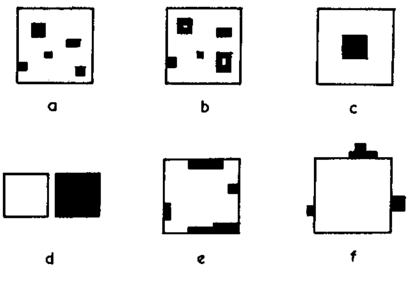

FIG. 8. Schematic representation of possible coke distributions in the catalysts (see text). Blocking of pore entries is implied in (e) but not in (f).

TABLE 3

Correlation of Coke Deposit Models with the Experimental Results

Model	TMA sorption capacity			EDA sorption		Kinetics of sorption
	Initial decrease with coking	Decrease at higher coke content	Coke content to prevent sorption	Saturation capacity increased then decreased	Acid sites	
a	X			X	X	
b				X	X	
c	X			X	X	X
d	X			X	X	
e	X	X	X	X	X	X
f	X	X	X			

some of the various possibilities. In (a) the carbon is deposited randomly, and coke grows from many centers within the crystal. Model (b) is similar, except that here local growth tends to seal off inaccessible parts of the zeolite. In (c) growth occurs from a single point within the crystal, and (d) would result from the same kind of growth pattern if carbon deposition is far more likely in some crystals than others. Deposits in (e) are formed just inside the crystal blocking channel entrances, whereas in (f) the carbon grows externally without restricting channel access. Table 3 summarizes the expected consequences of each type of deposition pattern for adsorption experiments of the kind carried out in this work.

The rapid initial loss of both sorption capacity and acid sites, observed both here and reported previously (*1*, *9*), means that some sealing off of adsorption spaces as in (b) must occur, though only some particularly active crystals, or parts of crystals, behave in this way. However, the EDA results show that some external coke deposits form, as evidenced by the changed acidity. The coke is therefore best described as being predominantly distributed as in (b), with a small contribution from external material as in model (f).

The following course of catalyst deactivation appears to be consistent with our results. Mobile, reactive intermediates are generated at the catalytically active sites. These may react with reactant or product molecules, or other intermediates. If the species so formed are sufficiently large, or shaped so as to prevent migration through the channel system, they will become localized and act as nuclei for the growth of further coke deposit. Where there are particularly active sites, or sites close together, higher concentrations of deposits can be expected to seal off some regions completely. Once this initial activity has decreased because of the removal of some or all of the more active regions, subsequent nucleation and growth will depend on the competition between these formation processes and the escape of potentially coke forming material from the crystal. This picture leads to the expectation that catalysts requiring the least frequent regeneration will have a relatively low density of active sites and small crystallite size.

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