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Pore Probe: A New Technique for Measuring the Concentrations of Molecules inside Porous Materials at Elevated Temperatures

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The pore probe technique allows us to measure the absolute concentrations of molecules in zeolite pores at any temperature. Large, intermediate, and small pore zeolites were contacted with a feed consisting of several C_6 isomers. The amount of each isomer adsorbed by the various zeolites was measured at temperatures from 25 to 330°C. © 1986 Academic Press, Inc.

INTRODUCTION

"Pore probe" is a technique we have developed which allows measurement of the steady-state concentrations of compounds within the pores of materials even at temperatures near or at typical reaction conditions. With this technique, we can measure the absolute concentrations of every reactant and product in the pores. We developed this approach in order to accurately determine effective zeolite pore size limitations whether or not a reaction is occurring. Also, with this information, the reaction mechanisms of various processes can be better understood.

In this paper, we will outline the experimental technique of the pore probe method. We will then describe the characterization of several zeolitic materials using the technique.

METHODS

The pore probe method works by effectively removing the catalyst bed during an ongoing reaction; then the compounds in the pores can be extracted and analyzed (Fig. 1).

The material collected consists of molecules that were in the pores and molecules that were in the dead space. To minimize corrections, the experimental system (Fig. 2) is designed to incorporate a minimum amount of dead space relative to pore volume. For shape-selective zeolites the feed that is not in the pores can be accurately accounted for by including a compound in the feed which cannot enter the pores. Blank runs using materials with no pores can be used to measure the steady-state concentrations of all the feed components in the dead space and on the external surfaces. The amounts of pore-fitting compounds which are in these sectors are then calculated. For example, let us assume a feed with three compounds is used and the ratio of Compounds A, B, and C extracted in a blank run over a nonporous material is 3:2:1. Then a pore probe experiment is conducted on a material whose pores exclude Compound C, and the analysis shows A:B:C = 7:3:1. It can be then calculated that the ratio of A to B in the pores = 7-3:3-2 = 4:1.

Finally, the absolute concentrations of the hydrocarbons in the pores can be measured. We do this by adding an external standard to the material collected from the pores so that absolute amounts collected can be determined. Since the catalyst weight (g) and pore volume (cm^3/g) are known, the total pore volume is known; and concentrations can then be calculated.

EXPERIMENTAL

Experiments are run by flowing a mixture of helium and feed through the preheater, then over the catalyst sample (Fig. 2). Gas

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samples can be collected through the sampling septum to analyze the product stream. When the product stream reaches a steady state, a pore probe experiment is performed as follows. Valves A and B (Fig. 2) are switched simultaneously to terminate the flow of the helium/feed mixture and to start the flow of N_2 over the catalyst and past Valve B into the liquid N_2-cooled U-tube. The N_2 sweep is maintained for 20–60 min, depending on the material being tested. Controls with known amounts of appropriate compounds are used to establish the collection time and temperature. Valve B is then closed and the cooled U-tube is evacuated. The cooled U-tube is then isolated, and the sample is transferred *in vacuo* to a collection tube containing acetone. (Alternatively, adsorbed compounds are removed from the pores by injecting an inert solvent during the N_2 sweep. The latter technique is particularly useful if the porous material is catalytically active at the temperature needed to evacuate the adsorbed compounds.) Then, the collected samples are anlayzed by gas chromatography (GC) using an external standard. Samples which are not amenable to transfer *in vacuo* are diluted with a mixture of solvent and external standard in the U-tube and then removed for analysis.

RESULTS

In this paper, we describe two types of experiments. In the first type, adsorbed components from a C_6 feed mix containing *n*-hexane (nC_6), 3-methylpentane (3MP), and 2,2-dimethylbutane (22DMB) are measured using several porous materials. Zeolite shape selectivity and pore concentration effects as a function of temperature are determined with this technique. In the second type, pore probe experiments are done on materials at temperatures high enough for cracking reactions to occur. The behavior of feed hydrocarbons in pores during the course of the cracking reaction is examined with this technique. For the second type of experiments, in order to assure that the material removed from the pores does not react during the evacuation, the cool sweep gas flow is set at >100 ml/min to cool the catalyst quickly. Since the experiments are done at low conversions, the temperature drop stops the reactions. Also, a cool liquid can be added to quench the reaction. (See Experimental.) The results from these two experimental approaches are summarized in Tables 1 and 2.

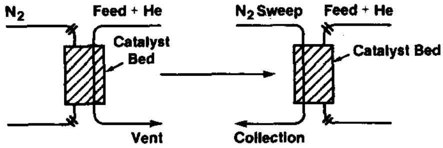

FIG. 1. Schematic of pore probe concept.

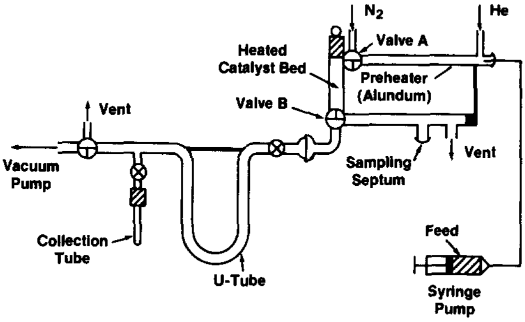

FIG. 2. Diagram of pore probe apparatus.

DISCUSSION

The concentrations of selected C_6 hydrocarbons in Y-zeolite are shown in Table 1.[1] The data show that Y-zeolite concentrates C_6 hydrocarbons from a He/hydrocarbon feed stream by a factor of 100 or greater, even at 330°C. The feed concentration in He is about 0.005 *M*. Y-Zeolite has a pore volume of 0.24 ml/g. At 330°C, 1 g of Na-Y condenses 16 μl or 0.12 mmol of hexanes from the feed stream. Therefore, the concentration of the hexanes in the pores is 0.5 *M*. This capillary condensation in zeolite mi-

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[1] The concentration of adsorbed hexanes in Na-Y is ca. 200 μl/g at room temperature (Table 1). This value obtained by the pore probe method agrees exactly with results obtained using standard gravimetric methods.

cropores has been postulated as an explanation for many catalytic properties of zeolites (*1*). Adsorption isotherms and NMR studies have been used to provide supporting data (*2*). Our method can now provide quanitative data of this type for many materials and feeds in order to test these postulates under actual reaction conditions.

Table 1 also gives pore probe results using a mixture of C_6 hydrocarbons as the feed for some shape-selective zeolites. The shape selectivities of ZSM-5 and erionite have been defined in terms of the constraint index (CI).[2] Small-pore zeolites such as erionite, which essentially crack only *n*-alkanes, have a CI $\gtrsim$ 40. Surface cracking probably keeps the value from being much greater. A medium-pore material such as ZSM-5 has a CI of $\approx$5–10. Y-zeolite, a large-pore zeolite, is not shape selective and has a CI of $\sim$0.5. The CI's are temperature dependent and are cited for the 300–400°C range.

Using CI to define the shape selectivity of a material suffers two deficiencies. First, acidity is required to drive the reaction and not all zeolites are sufficiently acidic to obtain the extent of reaction necessary for accurate CI determination. For example, it is difficult to measure the CI of a material in which hydrogen has been replaced by another cation which reduces the cracking activity. Second, the relative reactivity of 3MP and nC_6 may change depending on the acid strength and pore constraints imposed by the zeolite. Thus, the relative cracking rate of nC_6 and 3MP is not a measure of the relative concentration of nC_6 and 3MP in the pores.

The pore probe method avoids these difficulties. The technique uses a mixture of nC_6, 3MP and 2,2-dimethylbutane (22DMB) in helium as the substrate. The 22DMB does not enter small pores such as those in erionite and is used to calculate the amount of feed in the dead space and adsorbed on the surface. Since 22DMB enters pores such as those in ZSM-5 above room temperature, hexamethylethane (HME) was used as an internal standard. Experiments are usually run at temperatures at which the conversion is less than 10%, allowing the relative amount of nC_6, 3MP, and 22DMB in the pores to be determined (Table 1).

From the data, several observations can be made. Small-pore materials such as erionite and SSZ-16 are very selective for hexane adsorption. No 3MP could be detected in the pores although the sample was exposed to pure 3MP for over 8 h. Intermediate-pore ZSM-5 excludes neither singly nor doubly branched materials at higher temperatures, even when 10% nC_6 cracking occurs. [The room temperature values agree with those obtained by selective sorption studies (*4*).] Because both nC_6 and 3MP are in the pores at elevated temperatures and essentially only nC_6 cracks, it is likely that the high CI obtained for this zeolite is due to transition-state (TS) steric hindrance by the pores; i.e., the dominant cracking reaction is probably bimolecular, and only straight chains are small enough to easily align properly. The formation of a dimeric TS with a methyl-branched hydrocarbon is sterically hindered; thus, these molecules crack more slowly. (Although it is possible that the TS for unimolecular cracking of a branched hydrocarbon is too large, we think it is unlikely.) The possibility of a bimolecular reaction for straight-chain cracking is further evidenced by the cracked product distribution differences observed for nC_6, 3MP, and 22DMB using ZSM-5 (*5*). Highly branched 22DMB probably undergoes only slow unimolecular cracking in ZSM-5 and gives much more methane and ethane than nC_6 does. From the pore probe data, one would predict that unimolecular reactions will occur with much less selectivity. Indeed, straight and methyl-branched olefins crack at similar rates over

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[2] The shape selectivity of zeolites has been defined in terms of the constraint index (CI) by Frillette *et al.* (*3*). A 50/50 mixture of *n*-hexane (nC_6) and 3-methylpentane (3MP) is reacted over an acidic zeolite, and the CI is defined as log(fraction nC_6 remaining)/log(fraction 3MP remaining).

TABLE I

Pore Probe Results for Several Materials at Various Temperatures[a]

Material	T[b] (°C)	Hydrocarbon in pores, μl/g material			% Cracking[c]
		22DMB	3MP	nC_6	
Alundum powder[d]					
	25	2.4	4.0	4.9	0
	130	1.0	1.4	1.6	0
	240	0.6	0.8	0.8	0
	330	0.4	0.4	0.4	0
Amorphous silica alumina[e]					
	25	26	40	49	0
	130	2.6	3.1	3.9	0
	240	0.3	0.4	0.4	0
	330	0[c]	0	0	
H-Y[f]					
	25	22	54	74	0
	130	23	31	34	0
	240[g]	10.4	10.4	11.4	2
	240[g]	8.8	7.6	8.4	5
	280	4.0	3.8	4.2	5
	330	1.8	1.8	2.0	12
Na-Y[h]					
	25	16	68	106	0
	130	27	52	58	0
	240	18.8	24.4	25.4	0
	280	10.4	12.8	13.8	0
	330	4.8	5.6	6.0	0
H-ZSM-5[i]					
	25	1.6	4.0	112	0
	130	7.6	9.2	38.2	1
	130	7.0	9.6	37.4	0
	240	9.0	8.8	33.6	6
	280	4.6	4.2	7.0	8
Na-ZSM-5[j]					
	25	0	0	102	0
	130	5	8	35	0
	240	7	9	35.2	0
	280	5	6.2	12.2	0
Erionite[k]					
	25	0	0	28	0
	130	0	0	22	0
	240	0	0	14	0
	330	0	0	2	3
Na-SSZ-16[l]					
	25	0	0	38	0
	130	0	0	27	0
	240	0	0	19	0
	330	0	0	4.3	0
H-SSZ-16[m]					
	25	0	0	75	0
	130	0	0	30	0
	240	0	0	1.2	1.2

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[a] Conditions: feed rate = 1.2 ml/h; helium carrier gas flow = 35 ml/min. Feed is

ZSM-5 (*6*). Similar conclusions were drawn by Haag *et al.* in a study which employed ZSM-5 crystals of varying sizes to study the relative diffusivities of branched and straight hydrocarbons (*6*).

Details of molecular flow in zeolite pores

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nC_6/3MP/22DMB (33.7/33.4/32.2). Thus, the concentration of feed in He is 0.0043 *M*. Ten microliters of 2-methylpentane (2MP) is used as the external standard unless 2MP is formed during the experiment. In those cases, 10 μl of methylcyclopentane (MCP) is used. Acetone, ca 0.5 ml, is used as the diluent. The amount of material used in the catalyst bed is 0.5 g unless otherwise indicated. Analyses are done by gas chromatography (GC) using an FID detector. The weight percent values of the C_6's are uncorrected. Each run was done several times and the values obtained are reproducible to within 10%.

[b] The temperature in the catalyst bed is accurate to within ca. ±5°C.

[c] For some materials, cracking occurs at higher temperatures. The products are analyzed by collecting them during the run with a gas syringe, as described under Experimental. GC is used for analysis. For all the active samples, 0.5 g of catalyst was used, and the percentage cracking [wt% C_5^-/(wt% C_5^- + wt% C_6's)] value given is uncorrected for FID response differences.

[d] This material has no pores, and the values obtained indicate the amount of feed on surfaces and in the dead space.

[e] This is a typical cracking catalyst with about 0.4 cm^3/g of pore volume. The pores are about 50–200 Å in size. The amount of material on surfaces and in the dead space is subtracted out by using the values obtained for the alundum sample. A zero value indicates that the amount of hydrocarbon collected was equivalent to that collected when a material with no pores was used under the same conditions.

[f] This sample is low-sodium diuturnal Y-zeolite, a Linde stabilized zeolite. For the runs in which cracking occurs, about 0.2 mg of gas (mostly C_3 and C_4) is collected along with the C_6's. Some C_6 isomerization occurs. Any 2MP formed is added to the 3MP value. The small amount of 23DMB which forms is added to the 22DMB value.

[g] The 2% cracking run was done after the 5% cracking run. The decrease in activity is due to a small amount of coking.

[h] This material was made by exchanging H-Y (Note *f*) in 1 *M* $NaNO_3$ held at pH 10 (by adding NaOH) for 1 h at 100°C.

[i] This sample is from Linde (ELZ-105-6). Because 22DMB enters the pores, runs using hexamethylethane in the feed were done to accurately assess the dead space corrections. During the 250 and 280°C runs, ca. 1 mg of gas (mostly C_3 and C_4) was collected along with the C_6's. The 130°C run cracked 1% of the C_6 feed, but the higher temperature runs must deactivate some active sites because the rerun at 130°C (done after the 240 and 280°C runs) showed no cracking. During the 240 and 280°C runs, essentially only nC_6 was cracked.

[j] This sample is made by exchanging H-ZSM-5 (footnote *i*) in the same way as described in footnote *h*. Other samples of ZSM-5 and silicate were run, which gave slightly different results. Typical values for 22DMB/3MP/nC_6 are: 4/6/100 at 25°C, 6/16/40 at 130°C, and 8/10/16 at 240°C.

[k] This material is from Linde (ELZ-E-10). At 330°C, about 0.4 mg of gas (mostly C_3 and C_4) were collected along with hexane.

[l] This is a new zeolite synthesized by S. I. Zones at Chevron. It is made from H-SSZ-16, as described in footnote *h*; 0.3 g was used in the catalyst bed for the experiment. See U.S. Serial No. 425,786.

[m] Only 0.4 g of this material was used. At 240°C, 2.7 mg of gas was collected along with the *n*-hexane. Only nC_6 cracked. (Another sample gave 1% cracking at 240°C and the following values for nC_6: at 130°C, 29μl; and at 240°C, 8μl with ca. 1 mg gas.) Our collection method is quantitative for C_3^+ hydrocarbons, and most of the C_2's will also be collected. Even if most of the nC_6 in the pores cracked before it was evacuated, the amount of gas collected was only 2.7 mg. So, at most, only 3–4 mg of nC_6 was present in the pores.

at reaction conditons can be obtained using the pore probe technique. For example, the effects of creating low-molecular-weight products by cracking C_6 molecules in zeolites can be dramatic. Table 1 gives the pore probe results of experiments in which the concentration of nC_6 in the pores is measured as a function of conversion.

For ZSM-5, the cracked products (C_1–C_5) have only a small effect on the steady-state concentration of feed hydrocarbons in the pores. We conclude this by comparing the amount of C_6's in the pores of H-ZSM-5, which converts ca. 18% of the nC_6 at 240°C (total conversion is 6%; but only nC_6 is cracked), and Na-ZSM-5, which shows no perceptible cracking activity at 240°C.

Small-pore zeolites show different behavior. A new zeolite, SSZ-16, synthesized at Chevron has small pores ($CI \approx \infty$) which only admit nC_6. The hydrogen form is acidic enough to crack 3.6% of the nC_6 at 240°C. Erionite is inactive at this temperature, as is the sodium form of SSZ-16. Apparently, the production of a small amount of gas (C_1–C_5 hydrocarbons) by cracking markedly decreases the concentration of the nC_6 in the pores of SSZ-16 (Table 1). The gas products appear to be incapable of counterdiffusion with hexane in the small pores of the zeolite. Since the gases are not condensed by the pores as much as the C_6's, the amount of hydrocarbons in the pores decreases. For Y-zeolite, there is also some decrease in the amount of C_6's in the pores during cracking, but it is much less pronounced. Interestingly, the effect is larger for large-pore Y than for intermediate-pore ZSM-5. We have not yet tested whether or not this phenomenon is a function of pore dimensionality. Since reactant concentrations in the pores can affect the cracking mechanism (e.g., bimolecular versus unimolecular) which determines reaction rates and product distributions, information of this kind can be useful.[3]

TABLE 2

Pore Probe Results at 130°C for ZSM-5 Using Various nC_6/3MP Feed Mixtures[a]

Feed (nC_6/3MP)	Material in pore, μl hydrocarbon/g catalyst		$\frac{(nC_6/3MP)\ \text{Pores}}{(nC_6/3MP)\ \text{Feed}}$
	nC_6	3MP	
∞	80	0	—
0.48	40	25	3.3
0.24	25	36	3.0
0	0	49	—

[a] Conditions and accuracies are the same as given in Table 1. (Pure nC_6, 3MP, or a mixture of the two is fed at 1.2 ml/h in 35 ml/min of He.)

There are several other uses we have developed for the pore probe technique. We can obtain phase diagrams for a multicomponent mixture in a zeolite at elevated temperatures. By varying hydrocarbon concentrations in the feed mix, the relative concentrations of the feed components in the zeolite pores will change. Since we can measure the absolute amount of each component in the pores, we can plot the total amount of liquid in the pores versus the composition of the liquid. Table 2 gives some preliminary results for 3MP and nC_6 adsorption in ZSM-5. The degree of pore filling versus partial pressure of feed can also be measured at various conditions. The data given in Table 1 can be used to calculate the relative heats and entropies of adsorption of the feed components. Also, it is not necessary to wait for steady-state conditions to be reached before probing the pores. In this way, dynamic studies which measure the rates at which compounds replace each other in the pores can be done.

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[3] Thus, even though some small pore zeolites have large cavities at pore intersections where bimolecular cracking would not be sterically hindered, cracking may still occur unimolecularly because the gaseous products cause the reactant concentration to mimic the very low concentrations found in amorphous materials.

Finally, we are using the technique to elucidate the mechanisms of reactions other than hydrocarbon cracking. For example, at 240°C we have measured the steady-state concentrations of ethylbenzene and xylenes in the pores of ZSM-5. This allowed us to unravel part of the mechanism involved in the selective transalkyation of ethylbenzene, which we described in the previous paper.

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