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Catalytic Reaction and Fouling Effects on Intraparticle Diffusion

DAVID R. STOLL* AND LEE F. BROWN†

Department of Chemical Engineering, University of Colorado,
Boulder, Colorado 80302

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A pellet of gamma alumina with a unimodal pore structure and a mean pore radius of 47 Å was exposed to cycles involving counterdiffusing butenes and helium, counterdiffusing nitrogen and helium, and varying catalyst treatments. When butenes were present and the catalyst was active, the isomerization of 1-butene to *cis*- and *trans*-2-butene occurred. In the nonreacting nitrogen–helium system, the helium diffusion rate was about 11% less through an air-fouled catalyst than through the catalyst immediately after activation; it was about 13% less through the catalyst when butene-fouled than through the freshly activated catalyst. In the reacting butenes–helium system, the helium diffusion rate was about 17% less through the air-fouled catalyst than through the freshly activated catalyst; it was about 32% less through the butene-fouled catalyst than through the freshly activated catalyst. Only in the freshly activated catalyst was the helium diffusion rate in the reacting system predictable from the helium diffusion rate in the nonreacting system. It is proposed that the diffusion behavior differences between the reacting and nonreacting systems result from differences in adsorption characteristics of the fouled and active surfaces. The differences in adsorption characteristics in turn may cause different degrees of pore blockage. The experimental temperature was 154°C, and the pressure range was 1–2.5 atm for the butenes–helium system, and 1–13 atm for the nitrogen–helium system.

NOMENCLATURE

D	effective molecular diffusivity within porous material (cm^2/s)
D_K	effective Knudsen diffusivity within porous material (cm^2/s)
L	axial distance through pellet of porous material (cm)
M	molecular weight (g/g-mole)
N	flux of diffusing material [g-moles/(cm^2)(s)]
P	pressure (atm)
R	gas constant [(atm)(cm^3)/(g-mole)(K)]
T	temperature (K)
y	mole fraction or percentage of gas in stream
α	the quantity $[1 + (N_A/N_B)]$, dimensionless

Subscripts

A	of substance A [the lighter gas (helium)]
B	of substance B [the heavier gas (nitrogen or butene)]
He	of helium
L	condition at exit side of pellet
0	condition at entrance side of pellet

INTRODUCTION

Though there have been many studies of intraparticle gaseous diffusion in the absence of reaction, there have been few in the presence of reaction. But the latter area is probably economically much more important. Prior to 1962, investigators of diffusion in reaction systems relied on

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* Present address: 3M Company, 3M Center, St. Paul, MN.

† To whom correspondence should be addressed.

experiments with different sizes of pellets to determine effectiveness factors from which they could back-calculate effective diffusivities. Unfortunately there was no adequate diffusion theory with which they could compare their results at that time, so whether or not their results agreed with theory was not pursued. Current theory requires more data than presented by these early investigators, so their results cannot be compared with the current ideas. For example, Weisz and Prater (*1*) and Weisz and Swegler (*2*) did not present pore-size distributions of their catalysts. Johnson, Kreger and Erickson (*3*) gave detailed analyses of their catalyst, but their reaction system still represents too complex a system for present techniques of analysis.

Since 1962, the studies of diffusion in the presence of reaction have taken two paths. One path has compared the diffusion rates derived from kinetics studies with those calculated from theory. For example, Rao, Wakao and Smith (*4*) studied the ortho–parahydrogen shift over a bimodal catalyst, and compared the kinetic-based diffusivity with that predicted by the model of Wakao and Smith (*5*). Good agreement was obtained assuming no surface diffusion. Otani and Smith (*6*) used the same technique to study diffusion in the reaction of carbon monoxide over nickel-on-alumina. They found that the theoretical diffusion rates were 4 to 5 times the experimental rates. However, Steisel and Butt (7) showed that the method of Foster, Butt and Bliss (*8*) gave good agreement with the experimental values. Data obtained by Sterrett (*9*) on the ortho–parahydrogen shift in unimodal porous catalysts (average pore size of 20 Å) were compared with the predictions of four different models by Sterrett and Brown (*10*) and by Steisel, Foster and Butt (*11*). All the models predicted diffusivities around 40% below the experimentally observed value. Denisov, Zhidkov and Plygunov (*12*) studied the conversion of carbon monoxide with steam over a Fe–Cr oxide catalyst. They found the diffusion rate increased with catalyst activity. Only the abstract was available to the present authors and it gives no indication whether diffusion was faster or slower than predicted by present theories.

The second path used in recent studies of diffusion in the presence of reaction involves measuring the diffusion rates both in the presence of and in the absence of reaction, and using the results of the nonreacting system to predict transport rates in the reacting system. For example, the results of Omata and Brown (*13*), who reported nonreactive tortuosity factors for a catalyst almost identical with Sterrett's, can be used to predict Sterrett's hydrogen diffusion behavior. If this is done, the predicted diffusion rate is approximately 50% above the observed value, rather than the 40% below which occurred when the prediction was based on pore structure measurements combined with diffusion theory. This occurs because diffusivities predicted solely from pore structure measurements, with no diffusion data to supplement them, are reliable at best only within a factor of two (*14, 15*), and can be much worse for materials with abnormal pore structures (*13, 15*).

Using diffusion rates in the absence of reaction to predict those in the presence of reaction eliminates at least this one difficulty. In addition, some consistency begins to appear in the results of the different investigators. Dwyer *et al.* (*16*) studied the deuterium–neopentane exchange over palladium supported on silica–alumina particles. They gave no pore-size determination. From the reaction data they were able to calculate diffusivities of the neopentane. From hydrogen–nitrogen counterdiffusion studies with the catalyst, they were able to predict another value for the diffusion rate of neopentane. The latter diffusion rate was two to three times those derived in the reaction studies. Balder and Petersen (*17*) studied the hydrogenolysis of cyclopropane over a bimodal platinum-on-alumina catalyst and a platinum black catalyst. Kinetic diffusivities over the platinum-on-alumina were 25% below diffusion rates predicted from a counterdiffusion experiment. The kinetic diffusion rates for the platinum black were the same as those predicted from the counterdiffusion experiment. Their explanation was that fouling of the pores of the pellet reduced the calculated kinetic diffusion rate for the platinum-on-alumina catalyst. Wakao, Kimura and Shibata (*18*) studied the ortho–parahydrogen conversion over NiO on kieselguhr and over $CaO–Cr_2O_3$ catalysts. The NiO on kieselguhr was a bimodal catalyst with an average radius of about 50 Å. The $CaO–Cr_2O_3$ catalyst had a broad unimodal pore structure, average radius about 110 Å. Diffusion rates during reaction were about one-third those predicted from hydrogen–nitrogen counterdiffusion in a Wicke–Kallenbach experiment.

In summary, when the more reliable path for predicting diffusion rates was used, there was one system reported where the observed diffusion rates agreed with the predicted diffusion rates, and five systems where the observed rates were lower than predicted, ranging from 25% below predicted to one-third of the predicted value. So it appears that diffusion in the presence of reaction can be markedly less than in its absence, but it does not have to be. In the studies where the diffusion was significantly less than that predicted, the cause was not intensively investigated.

PROGRAM OF STUDY

More study of diffusion in the presence of reaction thus seems indicated. The present investigation used the second approach mentioned above, where diffusion studies were made both in the presence of and in the absence of reaction. One significant departure from previous work was that in our study one diffusing gas was the same in both the reacting and nonreacting systems. Helium was allowed to diffuse through the catalyst pellet when a reaction was occurring and when it was absent. In addition, both reacting and nonreacting systems were operated at the same temperature, so no temperature corrections were required for the comparisons. The helium diffusion rates were measured directly for both types of systems, so the comparisons could be as direct as possible. The goal was thus to compare the diffusion rates of helium in both reacting and nonreacting systems, with as little calculation as possible required to predict the diffusion behavior of the helium in the reacting system from its behavior in the nonreacting system.

For this a counterdiffusion apparatus, of the type usually attributed to Wicke and Kallenbach (*19*), was employed to measure the diffusion rates of gases during reaction. The Wicke–Kallenbach experiment consists of flowing two pure gases past opposing faces of a porous pellet. The circumferential surface of the pellet is sealed off, and the two gases are at the same temperature and pressure. Downstream from the pellet the compositions of the two streams are analyzed to determine the extent of crossflow (i.e., diffusion) of the two gases through the porous pellet. In one of the systems used, the two gases were 1-butene and helium; in the other, the two gases were nitrogen and helium. Within the pellet, the 1-butene could isomerize to form *cis*-2-butene and *trans*-2-butene. Thus in one system the diffusion rates of both helium and reacting butenes were measured directly. These results were compared with the helium and nitrogen diffusion rates measured in the nonreacting system.

This method of attack removed the need to use the reaction data to calculate diffusion rates, which complicates interpretation of the data of some previous investigators. For example, it eliminates the possible problems presented by dead-end pores. These pores, if they exist, do not contribute to the diffusion rates in counterdiffusion experiments, but they do contribute to the reaction rate and therefore to all diffusion rates based on reaction data.

Specifically, in our experiments a pellet of γ-alumina was exposed at 154°C (427 K) and varying pressures to cycles involving counterdiffusing butenes and helium, counterdiffusing nitrogen and helium, and catalyst treatment. By this technique, the behavior of the diffusion rates in both reacting and nonreacting systems was followed through activation of the catalyst and different kinds of fouling. The pressure range of the butene–helium counterdiffusion runs was 1–2.5 atm, being limited by the vapor pressure of the 1-butene in the cylinder. The pressure range of the nitrogen–helium counterdiffusion runs was 1–13 atm.

The complete sequence of counterdiffusion runs and catalyst treatments is presented in Table 1. Briefly, after pelleting and activation (described below), the alumina pellet was exposed to the atmosphere at room temperature for 12 hr. The alumina was shown to be completely inactive during the subsequent butene–helium counterdiffusion runs, and both these and nitrogen–helium diffusion measurements were made. The pellet was then removed and reactivated, and a further series of both butene–helium and nitrogen–helium counterdiffusion runs was made, punctuated by overnight blankets of gases which apparently did not affect the activity. The catalyst seemingly fouled only during the butene–helium runs. Finally, the catalyst was deliberately fouled by holding it overnight under a blanket of pure butenes at run temperature. Both nitrogen–helium and butene–helium runs were made on this fouled catalyst, and the series of experiments was terminated.

TABLE 1
SEQUENCE OF OPERATIONS[a]

Run no.	Catalyst treatment	Time (hr)
	Exposed to room atmosphere at 25°C	12
AFN1	Nitrogen–helium counterdiffusion	7
	Static nitrogen–helium blanket	17
AFB1	Butene–helium counterdiffusion	5
	Helium purge	20
AFN2	Nitrogen–helium counterdiffusion	7
	Static nitrogen–helium blanket	17
AFB2	Butene–helium counterdiffusion	5
	Catalyst reactivated by heating at 550°C	14
N1A	Nitrogen–helium counterdiffusion	8
	Static nitrogen–helium blanket	16
N1B	Nitrogen–helium counterdiffusion	7
	Static nitrogen–helium blanket	17
B1	Butene–helium counterdiffusion	6.5
	Helium purge	17.5
B1A	Butene–helium counterdiffusion	2
N2	Nitrogen–helium counterdiffusion	7
	Static nitrogen–helium blanket	15
	Nitrogen–helium counterdiffusion	2
B2	Butene–helium counterdiffusion	6.5
	Helium purge	15.5
B2	Butene–helium counterdiffusion	7.5
	Helium purge	16.5
N3	Nitrogen–helium counterdiffusion	6.5
	Catalyst aged under pure butene blanket	15
B3	Butene–helium counterdiffusion	5
	Static butene–helium blanket	19
N4	Nitrogen–helium counterdiffusion	8

[a] All temperatures 154°C except where noted. Starting material: activated gamma alumina.

EXPERIMENTAL APPARATUS AND PROCEDURE

Counterdiffusion Experiments

The counterdiffusion apparatus used in this investigation was originally constructed by Haynes (*20*) and extensively modified by Bell (*21*). Some description of the apparatus is given by Bell and Brown (*22*), and full details of the construction, calibration, operational procedures, and estimated error analyses are presented in Bell's thesis. The only significant change for this study was the addition of a chromatograph to analyze the butenes in the helium stream, and details of this modification are given by one of the present authors (*23*).

There were some changes required by alternating gas systems of widely different thermal conductivity. Different currents and signal amplifications were required for the butene runs and the nitrogen runs, so several dials on the thermal conductivity analyzer had to be changed before each run. Despite great care exercised in resetting all dials, significant changes in calibration were observed. This meant that the thermal conductivity cells which measured gas concentrations had to be recalibrated each run. This was done at a random time during the run; details are given in the thesis on which this paper is based (*23*).

A run was started with the gases being allowed to flow through the system for at least 1 hr to ensure complete flushing of the system and the stabilizing of the thermal conductivity measuring system. For operating at a particular pressure, the recorder indicated that within 5 min the system had reached steady state, and readings of flow rate and concentration were taken 15 to 20 min after the pressure was changed. Base-line drift on the thermal conductivity analyzer was monitored periodically.

Accuracy in determining fluxes through the pellet had been estimated by Bell (*21*) to be within ±2%, and his data were more consistent than that. While the scatter in this study was worse than Bell's, the error in the flux data is still believed to be below 2%. Errors in the chromatograph data were not estimated, and the data should be used only for general trends.

Pore Structure Determination

Mercury penetration of the alumina sample indicated that no significant volume of pores with radii larger than 200 Å were present. An Aminco Model 5-7119 15,000 psi porosimeter was used for this measurement. Because of this result, low-temperature nitrogen adsorption was considered sufficient for covering the entire range of pores within the material, and the pore-size distribution was determined by applying the method of Barrett, Joyner and Halenda (*24*) to the adsorption branch of the nitrogen isotherm. The flat-surface *t*-curve recommended by Broekhoff and de Boer (*25*) was used. The nitrogen adsorption apparatus was a Numinco-Orr surface area pore volume analyzer, Model MIC-101. Essentially it was as purchased from the manufacturer; some minor modifications made on this particular apparatus to improve its accuracy are described in the one author's thesis (*23*).

Pelleting of Alumina Catalyst

The pellets used in this study were made from Catapal SB alumina manufactured by Continental Oil Co. For a description of these aluminas see the company's brochure (*26*).

The alumina was received as a powder with an average particle size, according to the manufacturer, of approximately 40 μm. For this study a unimodal pellet was desired. In order that the voids between the powder particles would not make the pellets bimodal, the following recipe, adapted from that given by the manufacturer, was used to form a putty-like mixture.

Concentrated nitric acid, 0.36 g, was added to 11.5 g water. The dilute acid was added rapidly to 18 g alumina, and the resulting mixture was mixed for 3 min in a mortar. Mixing was continued for 27 min more while 4.3 g water were added.

The pellets were made in a small stainless steel press, with a piston 9.53 mm in diameter. The peptized alumina was then placed in the pellet press, and the pressure was raised slowly to about 270 atm, at which pressure the alumina "putty" started seeping out past the seals in the press. This pressure was held for 15 min, then released, and the alumina was pushed out of the mold using the top piston. The soft flexible 9.53 mm diameter extrudate was immediately cut into short pellets about 6.4 mm long. The cut pellets were air dried for several days, and as they dried they shrank to about their finished size, 7.1 mm in diameter by 4.0 mm thick. They were then heated slowly in an air furnace to 550°C, and held at this temperature overnight. After cooling they were filed down by hand with a fine metal file to their finished size. Finally they were heated twice more to 550°C. The reason for heating the catalyst three times was that this gave a more active catalyst than just one heating. The more active the catalyst, the more chance that effects of reaction on diffusion rate would be observable.

EXPERIMENTAL RESULTS

Catalyst Structure

Two pellets were made from the same batch of peptized alumina. One was used in the diffusion experiments, the other was used in the measurements of the physical properties and internal pore structure of the freshly activated catalyst.

Three nitrogen adsorption isotherms were run on the second of the above samples, and the results were indistinguishable. No desorption isotherms were run. The resulting pore-size distribution, obtained using

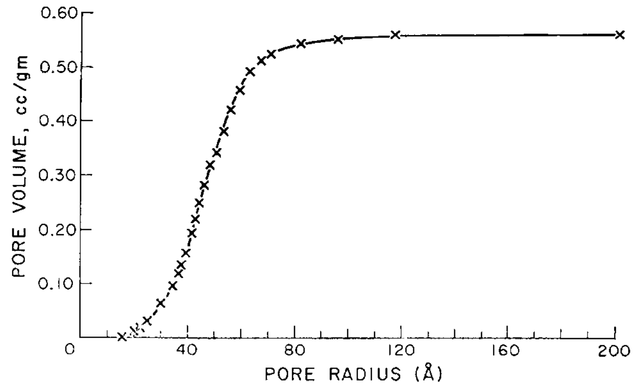

FIG. 1. Cumulative pore volume distribution.

the method mentioned earlier, is presented in Fig. 1. The catalyst has a unimodal pore-size distribution, with a mean radius of 47 Å. Other physical properties of the catalyst are presented in Table 2.

It was desired to have a catalyst with a mean pore radius of at least 50 Å, because it was in porous materials with mean pore radii less than this that Omata and Brown (*27*) noticed significant deviation from present intraparticle diffusion theory. Nevertheless, the 47 Å radius was considered satisfactory, since the operations of this study were carried out at 154°C, and at 146°C Omata and Brown has observed excellent agreement between diffusion theory and experiment using an alumina with a mean pore radius of 46 Å.

The surface area obtained from the pore-size distribution was 22% greater than the surface area from the BET method. The difference is within the range observed by Cranston and Inkley (*28*) and Broekhoff (*29*) when they also used the Barrett–Joyner–Halenda method to calculate the pore-size distributions from the adsorption isotherm. Three of the 35 samples reported by these investigators had differences between the two surfaces exceeding our 22% figure, so our catalyst does not appear to have had a particularly abnormal pore structure.

TABLE 2

PHYSICAL PROPERTIES OF CATALYST PELLET

Density of solid	3.32 g/cc
Pore vol	0.563 cc/g
BET surface area	217 m^2/g
Cumulative surface area from pore-size distribution	264 m^2/g
Mean pore radius[a]	47 Å
Av pore radius[b]	53 Å

[a] Defined as the radius where 50% of the pore volume is in pores with smaller radii, 50% in pores with larger radii.

[b] Defined as (2 × pore vol/BET surface area).

A nitrogen adsorption isotherm was also obtained using the pellet which had been used for the counterdiffusion, reaction, and fouling studies. Immediately after discharging the pellet from the counterdiffusion apparatus, it was examined for any visually apparent changes, crushed and placed in the adsorption apparatus, and degassed at 154°C overnight. Up through a relative pressure of 0.84, the adsorption isotherm was indistinguishable from that obtained on the unused, freshly activated catalyst discussed above. The points at relative pressures higher than this indicated about a 5% decrease in total pore volume. While this decrease is in the correct direction for a fouled catalyst, it is also possible that the two pellets could differ by more than 5% just from minor differences in pelleting pressures. As a result, no conclusions about the effect of fouling on structure can be drawn from the adsorption isotherms, except that any changes were probably not very drastic.

The visual appearance of the catalyst could not be followed during the experi-

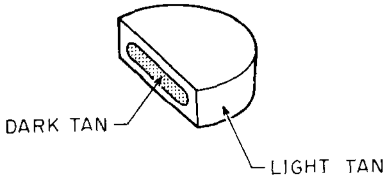

FIG. 2. Pellet after completion of studies.

ments because the pellet was encased in a stainless steel cell. Visual observations as to pellet conditions could be made only twice; when the pellet was reactivated, and when the pellet was removed upon completion of the studies. The originally pure white pellet after the air-fouled catalyst study was off-white in color. It returned to pure white upon reactivation. After the end of the active catalyst diffusion study, the catalyst remained under a helium–nitrogen blanket for 2 wk while the diffusion data were studied. When removed, the pellet was light tan. On cutting in half, it was found that the middle 1.5 mm of the pellet was dark tan. This dark band stopped short of the rubber gasket at the sides of the pellet. The coloring is probably caused by fouling but it appears a little confusing as to why it is distributed as shown in Fig. 2.

Catalyst Activity

The butene fraction in the helium stream was analyzed for the various butene isomers by gas chromatography. The catalyst activity during a particular run was judged by the 1-butene percentage of the total butenes; the higher the percentage of 1-butene, the lower the catalyst activity. This refers to the butenes in the helium stream; several chromatography samples were taken of the 1-butene stream flowing past the fact of the pellet, and they showed that conversion was negligible in that stream throughout the investigation.

In Figure 3 are presented the percentages of the different butene isomers in the butene fraction of the helium stream. In this figure, the data from one run is missing; the chromatograph column would not separate the *cis*- and *trans*-2-butenes during the first butene-helium run over the active catalyst (run B1).

Figure 3 shows that over the air-fouled catalyst, catalyst activity was essentially zero, as no 1-butene was converted. Following activation, significant conversion (almost 80%) took place. Apparently there was some deactivation during reaction, as displayed during runs B1A and B2. But there was no apparent deactivation between runs B1A and B2′, or between B2′ and B2, when the catalyst was exposed only to nitrogen and helium. Mere exposure to nitrogen and helium was not regarded as significant catalyst treatment therefore, and is ignored in the graphs and tables. Between runs B2 and B3, serious deactiva-

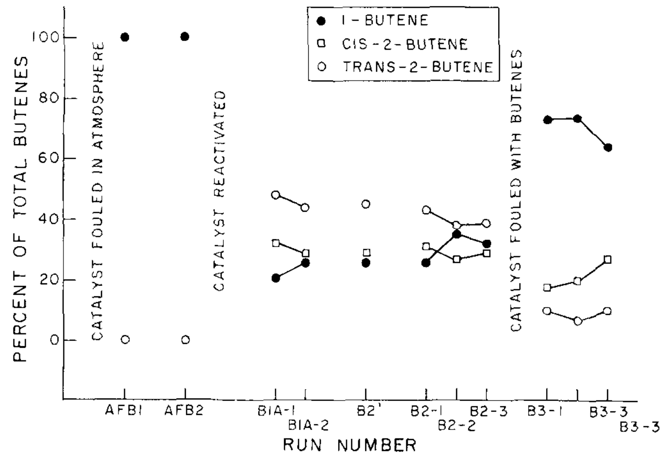

FIG. 3. Analyses of butene fraction of helium-rich stream.

tion occurred, as was expected from holding the catalyst overnight under a blanket of only butenes at 154°C. Some improvement in catalyst activity apparently occurred during the reaction involving counterdiffusing butenes and helium the next day, as shown by the behavior of run B3. As mentioned earlier, the chromatograph data should only be used for general trends, as no consistency or accuracy measurements were made to test the column used in taking the data.

Thus counterdiffusion behavior was measured using both nitrogen–helium and butene–helium systems over an air-fouled catalyst with negligible activity, then over an active catalyst of slowly decreasing activity, and finally over a seriously fouled catalyst.

The ratio of *cis*- to *trans*-2-butene in the butene fraction also changed radically during the operations over the catalyst, indicating a marked alteration in catalyst selectivity over this period. This can possibly be accounted for simply by the reduction in catalyst activity. Hightower and Hall (*30*) indicate most *trans*-2-butene is formed from *cis*-2-butene, so the much greater reduction in amount of *trans*-2-butene in the helium stream may be the result of less *cis*-2-butene formed early in the reaction zone.

Nitrogen–Helium Flux Ratios

Present theory of gaseous diffusion within porous materials predicts that under the conditions of the Wicke–Kallenbach experiment, irrespective of temperature or total pressure, the ratio of the fluxes of the counterdiffusing gases should be

$$\frac{N_A}{N_B} = -\left(\frac{M_B}{M_A}\right)^{1/2}. \tag{1}$$

Here, the subscript A refers to the lighter gas (helium) and B the heavier gas (nitrogen or butene). The theoretical values of these ratios are −2.65 for the nitrogen–helium system, and −3.74 for the butene–helium system. This ratio has been shown to be reasonably valid at all temperatures for materials with average pore radii above approximately 50 Å by many investigators; their work is reviewed and some additional data are presented by Omata and Brown (*27*).

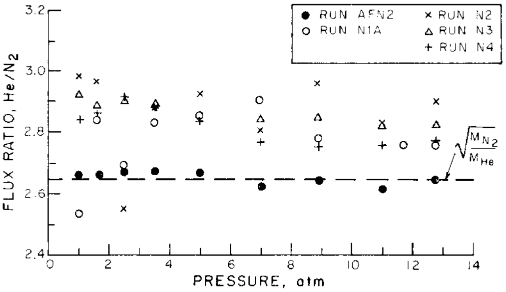

FIG. 4. Helium–nitrogen flux ratios.

The flux ratios for the nitrogen–helium runs are presented in Fig. 4. It can be seen from this figure that the flux ratio observed when counterdiffusion took place over the air-fouled catalyst almost exactly matched the theoretical value over the entire range of pressures investigated. There is some scatter in the flux ratios observed after activation was carried out, but the ratio tends to be about 7% higher than the theoretical value, and still independent of pressure. Any trend with processing and fouling is obscured by the scatter.

Minor differences in the flux ratio such as observed here were observed by Omata and Brown (*27*) for different catalysts, but they did not investigate the cause of these differences (if indeed they really exist).

The data from two runs are missing from Fig. 4; a leak just after the diffusion cell occurred during run AFN1, so the results from this run were discarded, and the helium fluxes from run N1B appeared to be abnormally low, so the results from this run were discarded also.

Nitrogen–Helium Fluxes

Since there is no surface diffusion and the mean pore size is 47 Å, the work of Omata and Brown (*27*) indicates that the data should obey the dusty-gas equation:

$$N_A = \frac{PD_{AB}}{RLT\alpha} \ln\left[\frac{1 - \alpha y_{A0} + (D_{AB}/D_{KA})}{1 - \alpha y_{AL} + (D_{AB}/D_{KA})}\right]. \tag{2}$$

This equation can be treated as an equation with two unknowns, D_{KA} and PD_{AB}, where D_{KA} and D_{AB} are the effective Knudsen diffusivity and effective bulk diffusivity, respectively. Through use of nonlinear regression techniques, the equation can be fitted to the experimental data. A sensitive manner of showing the results comes from plotting the normalized error [(theoretical value − experimental value)/experimental value] as a function of pressure. This is done in Fig. 5 for the helium flux of a typical run.

The agreement between theory and experiment is not good. The theoretical fluxes are much lower at low pressures than observed, increase rapidly to above the observed, and then gradually decrease to below the observed. Of special importance is the pressure range of the helium–butene study, from 1 to 2.5 atm. There the slope of the graph is very steep, indicating serious failure of the theory. The behavior shown by Fig. 5 was observed in all the nitrogen–helium experiments.

The behavior is similar to that observed by Omata and Brown for their 24 Å radius material. This behavior is thus indicative of the presence of an average pore radius smaller than that indicated by the pore-size distribution. There is the possibility of constricted pores; abnormalities in diffusion behavior have been ascribed to their presence (*15*). The comparison of the BET and cumulative surface mentioned earlier, while within limits observed by others, was still not particularly good and was in the direction to be expected in the presence of constricted pores (*15*). Whatever the reason, use of the dusty-gas diffusion equation for analysis of the various diffusion data is precluded in the present study.

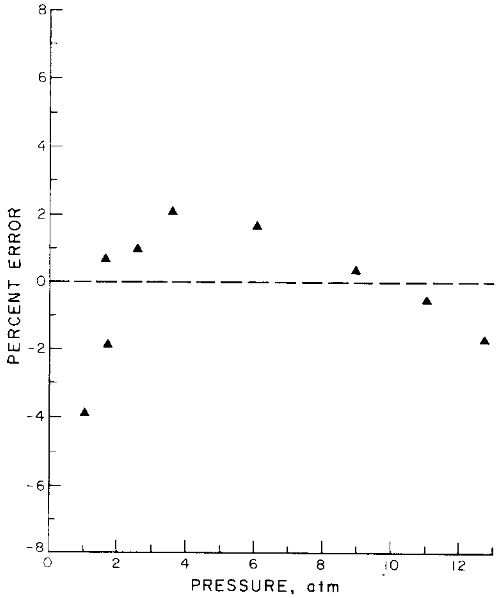

Fig. 5. Comparison of dusty-gas diffusion theory with behavior of helium flux in nitrogen–helium system; run N3.

It had been intended to determine values of the effective Knudsen and bulk diffusivities for the helium and the nitrogen from the nonlinear regression of the data from the various runs, and examine how these diffusivities varied with the different kinds of fouling and catalyst activity. Unfortunately, inapplicability of present diffusion theory excludes this approach. What can be done is to look at the changes of the fluxes during the operations over the catalyst, and see how these changed with the catalyst treatment and processing.

This is done in Table 3. It can be seen that the conditions did not vary much from run to run, and so the absolute values of the flux are directly comparable. In the low-pressure runs the helium flux in the air-fouled catalyst was 10% below that in the reactivated catalyst, indicating that one effect of reactivation was to increase the size of the pores or remove some plugs within the pellet. The helium flux in the air-fouled catalyst was 12% below that in the reactivated catalyst at the highest pressure. Several hours of carrying out the reaction resulted in a decrease of 7.4% in the low-pressure helium flux, and a decrease of 8.0% in the high-pressure helium flux. The fouling caused by holding the catalyst overnight under a pure butene blanket at 154°C caused an additional decrease of 2.9% in the low-pressure flux and 6.3% in the high-pressure flux. Overall, processing caused about a 12% decrease in the low-pressure helium flux and a 14% decrease in the high-pressure flux. It is

TABLE 3

Changes in Helium Flux with Catalyst Treatment (Nitrogen–Helium Counterdiffusion)

Run no.	Immediate pretreatment	Low pressure runs				High pressure runs			
		P	y_{He0}	y_{HeL}	$N_{He} \times 10^6$	P	y_{He0}	y_{HeL}	$N_{He} \times 10^6$
AFN2	Catalyst fouled in atmosphere; butene–helium counterdiffusion	1.02	1.77	99.21	1.22	12.69	1.68	98.27	9.83
N1A	Catalyst activated	0.97	1.63	99.23	1.36	12.6	1.73	98.45	11.2
N2	Butene–helium counterdiffusion	1.07	1.74	99.27	1.30	12.8	3.18	97.22	10.20
N3	Butene–helium counterdiffusion	1.03	1.66	99.17	1.26	12.7	4.00	98.41	10.3
N4	Butene blanket overnight at 154°C; butene–helium counterdiffusion	1.07	1.51	99.17	1.22	12.8	3.42	98.17	9.59

concluded from these results that the catalyst fouling decreased the effective size of the pores or plugged some of the pores through which diffusion was occurring.

It must be realized that if there was a decrease in pore size, the decrease did not have to be very great for the observed effect to occur. If cylindrical pores are assumed, then the Knudsen diffusion flux is proportional to the radius of the cylinders cubed (if the number of cylinders is constant). A decrease in average pore radius from 50 to 48 Å would account for a 12% decrease in diffusion flux. Although the data shown in Table 3 were taken in the transition region between Knudsen and molecular diffusion, they were still rather close to the Knudsen region. Less than a monolayer of fouling material would thus explain the decrease in helium diffusion flux with catalyst fouling.

Butene–Helium Flux Ratios

Theory predicts that the ratio of helium flux to butene flux should be −3.74. Figure 6 shows the actual fluxes obtained in this study. There is scatter in the data, and no conclusions can be drawn from changes of flux ratio with catalyst treatment. But the ratios observed are consistently below the theoretical value, with an average value of approximately 3.35, 10% below the theoretical value.

Bell (*21*) has ascribed a flux ratio below the theoretical value to the presence of a mobile phase, which may or may not be diffusing. Some surface diffusion of the butenes may have been present, but definite indication of this from the change of flux ratio with pressure (it should show a steady decrease with increasing pressure if surface diffusion is present) is obscured by the scatter in the data. Nevertheless, the change of the flux ratio in the freshly activated catalyst from 7% above the theoretical value in the nonreacting system to 10% below the theoretical value in the reacting system does indicate the high probability of some mobility in the adsorbed butenes.

Butene–Helium Fluxes

Since diffusion theory cannot be applied, the values of the fluxes in the butene–

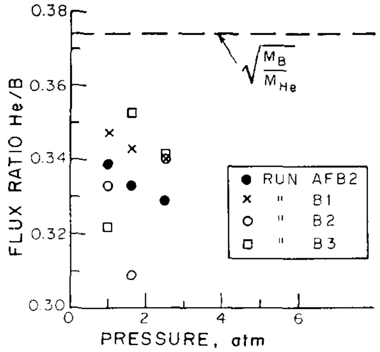

Fig. 6. Helium–butene flux ratios.

helium reacting system must be compared in the same fashion as the fluxes in the nitrogen–helium nonreacting system. This is done in Table 4.

Table 4 shows that the behavior of the helium flux in the butene–helium runs is qualitatively similar to that observed in the nitrogen–helium runs, i.e., activation of the air-fouled catalyst resulted in an increase in the helium flux, which thereupon declined steadily as the catalyst fouled. Quantitatively, though, the fluxes indicate significant differences between the reacting and the nonreacting systems. The increase in the helium flux in the butene–helium system upon activation of the catalyst was 21%—almost twice the 11% increase observed in the helium flux in the nitrogen–helium system upon activation of the catalyst. The overall decrease in the helium flux in the reacting system during fouling was 32%—almost three times the 12% decrease observed in the helium flux in the nonreacting system during fouling.

The cause of this rather large decrease in flux must have been partially a temporary one, otherwise the decrease in the nitrogen–helium fluxes would about equal that of the butene–helium fluxes. A change in possible surface flux of the butenes because of changing surface characteristics of the catalyst was considered. Bell (*21*) has analyzed situations of this type, and following his reasoning, this possibility was rejected. An increase in surface-diffusing butenes would be required to cause the decrease in gas-diffusing helium, and this did not occur. The flux ratios would have changed markedly in this case, and they did not.

A possible explanation is a change in the amount of adsorbed butene. It is possible that fouling of the catalyst provides more sites for the adsorption of butene. Clark and Finch (*31*) have shown that butenes adsorb on polymer deposited on silica–alumina catalysts, and it seems reasonable that the same might be true of alumina. Thus the reduction of the gas-phase diffusion rates with fouling may be partially a function of the amount of adsorbed butene, and the amount of adsorbed butene may increase with catalyst fouling. The increased amount of adsorbed butene would either decrease the effective pore radius or plug some of the smaller pores, decreasing the diffusion rate.

Prediction of Helium Flux in Reacting System

It is impossible in the present system to use the effective diffusivities obtained from the nonlinear regression of the nitrogen–helium counterdiffusion data to predict the behavior of the helium in the butene–helium system. However, at the lowest pressure, the diffusing helium approaches Knudsen flow. At 1.05 atm, 154°C, and in a pore of 47 Å radius, the Knudsen number (ratio of mean free path to diameter of pore) of a helium molecule in otherwise pure butene is 14, in otherwise pure nitrogen is 19, and in pure helium is 28. These then cover the span of the Knudsen numbers of helium at the lowest pressure in the systems reported here. Since Knudsen numbers above 10 indicate essentially Knudsen flow (*32*), the interaction of helium with other molecules in the gas phase should be quite negligible. For this reason, the helium flux should be identical

TABLE 4

CHANGES IN HELIUM FLUX WITH CATALYST TREATMENT (BUTENE–HELIUM COUNTERDIFFUSION)

Run no.	Immediate pretreatment	P	$y_{\mathrm{He}\,0}$	$y_{\mathrm{He}\,L}$	$N_{\mathrm{He}} \times 10^6$
AFB2	Catalyst fouled in atmosphere; butene–helium counterdiffusion	1.03	1.45	99.32	1.12
B1	Catalyst activated	1.08	1.62	99.46	1.35
B2	Butene–helium counterdiffusion (run B1)	1.08	1.77	99.45	0.989
B3	Butene blanket overnight at 154°C	1.07	1.25	99.60	0.920

in both the reacting and nonreacting systems at the lowest pressures.

A comparison of the helium fluxes for the comparable runs in Tables 3 and 4 shows that in the air-fouled catalyst, the helium flux was 8% less in the butene–helium system than in the nitrogen–helium system. In this case both of these systems were nonreacting. In the freshly activated catalyst, the helium fluxes were almost identical. As the catalyst fouled, the helium flux in the reacting system dropped lower and lower below that in the nonreacting system, until over the seriously fouled catalyst, the helium flux in the reacting system was 25% below that in the nonreacting system.

Thus in our system there were observations qualitatively identical with those of the earlier investigators mentioned at the beginning—observed diffusion rates in reacting systems may be equal to or less than those calculated from nonreacting systems using the same catalyst. The differences, when observed, can range from slight to drastic.

The behavior observed in the present investigation results, of course, from the different flux changes observed with catalyst treatment in the reacting and nonreacting systems. If it is accepted that the cause of the different behavior of the helium fluxes in the reacting and nonreacting systems is different adsorption characteristics of the fouled and unfouled surfaces, then it appears that the freshly activated (and highest activity) catalyst adsorbs the least amount of butenes. This is reinforced by the freshly activated catalyst having the same low-pressure helium flux for both the reacting and nonreacting systems. The fouled catalysts all presumably adsorbed butenes in varying amounts which were sufficient to affect the helium flux within the catalyst pellet.

CONCLUSIONS

In a nonreacting nitrogen–helium system, the diffusion rate of helium was about 11% less through an air-fouled catalyst than through a reactivated catalyst; it was about 13% less through a butene-fouled catalyst than through the reactivated catalyst. It is postulated that the fouling decreased the average pore radius of the catalyst slightly or plugged some of the pores, and activation enlarged the pores slightly.

In a reacting butene–helium system, the diffusion rate of helium was about 17% less through the air-fouled catalyst than through the catalyst after reactivation; it was about 32% less through the butene-fouled catalyst than through the reactivated catalyst. It is proposed that the cause of the differences between the diffusion behavior of the reacting and nonreacting systems lies in differences in butene adsorption characteristics of the fouled and unfouled surfaces.

Only for the reactivated catalyst was the helium diffusion rate in the reacting system predictable from the helium diffusion rate in the nonreacting system. If different adsorption characteristics of fouled and unfouled surfaces are the causes of this, then this indicates that the smallest amounts of butenes are adsorbed on the most active surface.

The adsorbed butenes probably possess some mobility on the catalyst surface.

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