In Situ PFG NMR Study of Intracrystalline Diffusion during Ethene Conversion in ZSM-5

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Pulsed field gradient (PFG) NMR spectroscopy has been applied to measure the self-diffusivity of an inert probe species *in situ* during a zeolite-catalyzed reaction. Specifically, ^{19}F PFG NMR was used to measure CF_4 intracrystalline mobility during ethene conversion in H-ZSM-5 as a function of reaction time in sealed glass samples. CF_4 was shown to be a suitable probe species, and its mobility was seen to be sensitive to changes in the composition of the reacting system with time for the conversion of ethene in H-ZSM-5. Also, the self-diffusivity of CF_4 in well-defined nonreacting mixtures could be correlated with the mobility and changing composition of the reacting system. Studies of the reaction kinetics were performed by ^{13}C MAS NMR and with a recirculation reactor. At low temperatures (approx. 373 K) ethene is converted mainly to paraffins. The gas-phase products observed in the recirculation system ranged from C_2 to C_7 alkanes.   © 1996 Academic Press, Inc.

INTRODUCTION

It is well known that mass transfer can play a very important role in zeolite catalysis (1–3). If diffusion effects are large, it can lead to changes in the observed reaction rate or selectivity or both. Understanding diffusion in zeolites is thus critical to the development of zeolite catalytic processes. Nevertheless, direct *in situ* measurements of diffusion under reaction conditions are almost nonexistent in the literature. Nießen *et al.* (4, 5) applied an FTIR technique to measure uptake rates of benzene and ethylbenzene at 395 K, where the zeolite catalyst, H-ZSM-5, was intermittently coked *in situ* at higher temperatures by the dealkylation of ethylbenzene or by the conversion of ethene. The coking temperature was seen to play an important role in how the coke affected the diffusivity of benzene or ethylbenzene. This was attributed to differences in the nature of coke formed at different temperatures (6). Hong *et al.* (7) demonstrated that Fourier transform pulsed field

gradient (PFG) NMR spectroscopy allows the direct measurement of the self-diffusivities of the individual reactant and product species during catalytic reactions. They applied the technique to study the conversion of cyclopropane to propene in zeolite X. The reactions were carried out in sealed glass sample tubes, and the self-diffusivities of cyclopropane and propene were simultaneously determined as a function of conversion as the reaction proceeded. For this system, the self-diffusivities of the reactant and product species were found to be essentially the same, and they remained constant as the composition of the system evolved during the course of the reaction. It was found that for such a system the diffusivities under reaction conditions could be extrapolated from the diffusivities determined at lower temperatures where no chemical reaction took place.

PFG NMR is well suited for *in situ* diffusion measurements during chemical reaction, as it can be performed over a range of temperatures that includes temperatures of interest in catalysis and it allows one to measure the mobilities of individual species in a mixture (8, 9). This latter feature is particularly important, since catalysis inherently involves multicomponent systems. PFG NMR can be applied to multicomponent systems in two ways. The first is Fourier transform PFG NMR, used by Hong *et al.* (7), for example. The NMR spin echo is Fourier transformed, and if the chemical shifts characteristic of individual species are sufficiently different, separate peaks can be resolved for the various adsorbates in the system. The attenuations of the various peaks with increasing applied field gradient pulse intensity yield the self-diffusivities for the corresponding chemical species, similar to the way in which the attenuation of the untransformed spin echo yields the diffusivity in the usual single-component PFG NMR experiment. The second way in which PFG NMR can be applied to multicomponent systems is by preparing the sample such that only one species contains the nucleus to be observed by NMR. In this work we have adopted the latter approach.

We report here ^{19}F PFG NMR measurements of the self-diffusivity of tetrafluoromethane (CF_4) during the conversion of ethene in H-ZSM-5. The CF_4 molecules do not

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participate in the reactions of the ethene but serve as an inert probe species, whose mobility can be considered as representative of that of other small molecules in the system. While this approach does not provide a direct measurement of reactant and product diffusivities, as in the work of Hong *et al.* (7), it does provide certain experimental advantages. First, it can be applied even to complex reactions, where Fourier transformation of the spin echo would not be able to provide distinguishable peaks for the many reaction participants involved. Second, for certain probe species the method can be used even when the reactants or products have diffusivities that are beyond the range of PFG NMR. The third advantage concerns the speed with which the experiment can be carried out. The amount of time required for each experiment determines the number of diffusivity measurements that can be performed during the course of the batch reaction. In Fourier transform PFG NMR in zeolite systems, it is common to accumulate the spin echo several thousand times (7, 9). This means that a single PFG NMR measurement could last several hours, depending on the repetition time of the accumulations (dictated by the T_1 relaxation time). The *in situ* measurements of CF_4 mobility reported here, on the other hand, were generally performed with 16 signal accumulations, and an entire PFG measurement could be completed in about 15 min.

Due to the importance of ethene as an intermediate in the methanol-to-gasoline process, ethene conversion on H-ZSM-5 has attracted both industrial and academic interest (10–17). ^{13}C NMR investigations have shown that ethene on H-ZSM-5 is converted into strongly adsorbed olefinic oligomers starting near room temperature. These products are highly reactive and convert to paraffins at higher temperatures or reaction times. In order to compare the reactivity of our zeolite samples with those in the literature, we made our own ^{13}C MAS NMR measurements. Additionally, we performed recirculation reactor investigations to compare with the NMR studies and to provide additional information on the product composition that is not easily obtained from NMR, such as the carbon number distribution of the alkanes formed.

EXPERIMENTAL

The zeolite samples used are described in Table 1. Silicalite, H-ZSM-5 (I), and H-ZSM-5 (II) were synthesized by the method of Mueller and Unger (18). The samples were calcined in nitrogen at 813–823 K, followed by air calcination at the same temperature. The calcined samples were ion exchanged twice with a large surplus of a 1 *N* aqueous solution of NH_4NO_3 in order to remove traces of alkali cations. The samples were then calcined in a flow of dry nitrogen at 813 K to obtain the H^+ form. Chemical analysis was done after dissolving the zeolites in HF (10 wt% in

TABLE 1

Zeolite Samples

Name	Si/Al	Size (μm)
Silicalite	480	$100 \times 20 \times 20$
H-ZSM-5 (I)	41	$100 \times 20 \times 20$
H-ZSM-5 (II)	20	$80 \times 20 \times 20$
H-ZSM-5 (III)	38	~ 0.1

water) using atomic emission spectroscopy with inductively coupled plasma. Crystal size and morphology were determined by scanning electron microscopy. H-ZSM-5 (III) was a commercial product obtained from P.Q. Zeolite B.V.

For the studies in the recirculation system, 0.1 g of zeolite sample was placed into a quartz reactor and pretreated *in situ* at 723 K for 2 h in nitrogen flow (3 liters/h). After cooling to reaction temperature (373 K), the system was evacuated and subsequently filled with ethene to the desired pressure and then with nitrogen until atmospheric pressure was reached. The recirculation pump was started, marking the beginning of the experiment ($t = 0$). Products were analyzed by an on-line gas chromatograph equipped with a PONA capillary column and flame ionization detector.

In addition to the reactor studies, we investigated the reactivity of ethene in H-ZSM-5 (II) using ^{13}C magic-angle spinning (MAS) NMR. Samples were prepared by heating 8 mm of zeolite placed in glass tubes 5 mm in diameter. The temperature was increased to 673 K at a rate of 10 K per hour under vacuum. Samples were maintained at 673 K at a pressure less than 0.01 Pa for 24 h and then cooled to room temperature. A known quantity of sorbate was next introduced from a calibrated gas volume by cooling the sample in liquid nitrogen. The samples were then sealed off. Ethene–$^{13}C_2$ (99% ^{13}C) from Cambridge Isotopes was used without further purification. Since ethene is known to react in H-ZSM-5 at room temperature (15), samples were stored in a refrigerator at 258 K prior to the measurements. The ^{13}C MAS NMR measurements were performed on a Bruker MSL 300 spectrometer. Samples were placed in the spectrometer and heated to the temperature of interest. All spectra were recorded at the reaction temperature by means of single pulse excitation with high-power proton decoupling at spinning rates of ca. 4 kHz and pulse delays of 5 s. Concentrations were obtained from the areas under the peaks after Fourier transformation.

Samples for the PFG NMR experiments were activated in the same manner as the MAS NMR samples, but tubes of 8 mm diameter were used. In order to ensure mechanical stability of the zeolite material when subjected to the mechanical pulses accompanying the pulsed field gradients, we used sample tubes containing a capillary and filled only the part below the capillary with zeolite (19). Intracrystalline self-diffusivities were measured with ^{1}H, ^{13}C, and ^{19}F pulsed

field gradient NMR (2, 20) on a home-built spectrometer operating at a proton resonance frequency of 400 MHz (21). The spectrometer can supply pulsed field gradients up to 24 T/m with rise and fall times (10–90%) on the order of 100 μs. Each measurement was performed by varying the applied gradient strength g (e.g., from 0 to 24 T/m) with a fixed pulse duration δ and fixed observation time for diffusion Δ. The self-diffusivities D_s were obtained from the attenuation of the NMR spin echo ψ with increasing g,

$$\psi(\delta, g, \Delta) = \exp[-\gamma^2 \delta^2 g^2 D_s(\Delta - \delta/3)], \quad [1]$$

where γ is the gyromagnetic ratio of the nucleus under observation (2, 20).

RESULTS AND DISCUSSION

Results of the ^{13}C MAS NMR kinetics experiments on H-ZSM-5 (II) are shown in Fig. 1, where ethene concentration is plotted as a function of reaction time at 330 and 343 K. From the linearity of the plot, the disappearance of ethene in the sealed sample tubes is seen to be well described by first order kinetics. The ^{13}C MAS NMR spectra (not shown) are similar to those reported in the literature (11, 14–16) and indicate that at these temperatures the reaction products are alkanes.

The distributions of gas-phase products observed in the recirculation reactor are presented in Fig. 2 for zeolite H-ZSM-5 (III). The small crystal sample was used to avoid any interference of mass-transfer effects. Results are shown
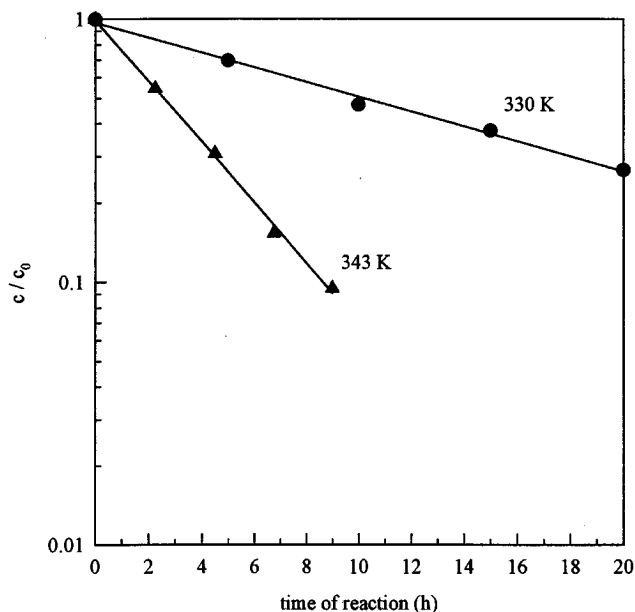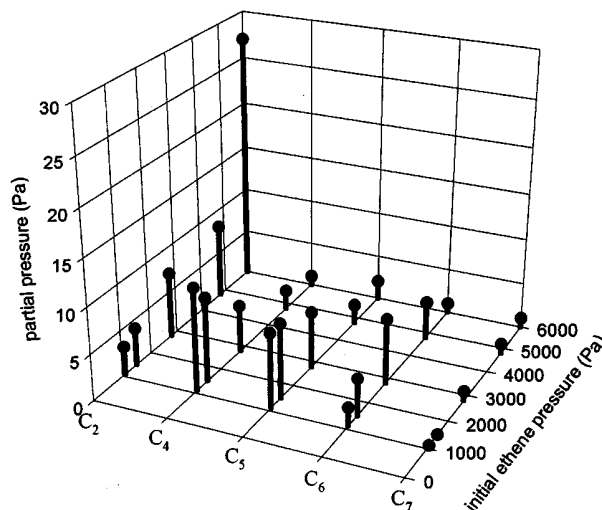

FIG. 2. Distribution of gas-phase products observed in the recirculation reactor system at 373 K and a reaction time of 150 min for ethene on H-ZSM-5 (III). The products range from C_2 to C_7 and are moslty alkanes.

for a temperature of 373 K and 150 min reaction time. The products observed are mostly alkanes and are in the C_2 to C_7 range. Interestingly, we observed mainly olefinic products in a flow reactor, in contrast to the paraffinic products observed for the recirculation system. Vedrine *et al.* (12) also report olefinic products in their flow reactor studies. Recall that the reaction is thought to proceed first by ethene oligomerization and then further conversion of the oligomers. Differences in gas-phase partial pressure, residence time, and conversion may account for the different products seen with the two reactor configurations. The recirculation system, however, corresponds more closely to the conditions in the NMR experiments and also yields alkanes as seen by MAS NMR.

An Arrhenius plot of the self-diffusivity of ethene in silicalite is shown in Fig. 3 for a loading of 12 molecules per unit cell. We present results for the high-silica form, silicalite, rather than H-ZSM-5 because of the reactivity of ethene in H-ZSM-5 even at room temperature. The difference in Si/Al ratio between these two isostructural zeolites has been shown to have some effect on the diffusivity of a polar adsorbate like water (22), no significant effect for methane (22), and only a small effect for ethanol (23). We therefore expect the diffusivities of ethene in any of the zeolites considered in this work to be very nearly identical. The measurements for ethene in silicalite proved to be difficult due to the short relaxation times for ethene in silicalite, which are even shorter than those for alkanes in this zeolite. The results shown were obtained using ^{13}C PFG NMR with the stimulated echo sequence and observation times Δ of 4 ms. The spin echoes were accumulated 128 times. The self-diffusivities and the activation energy are similar to those in the literature for the corresponding saturated species, ethane (2).

FIG. 1. Ethene concentration as a function of time as determined by ^{13}C MAS NMR on H-ZSM-5 (II) at 330 and 343 K. Samples were initially loaded with 12 molecules of ethene per unit cell (c_0) and sealed before reaction.
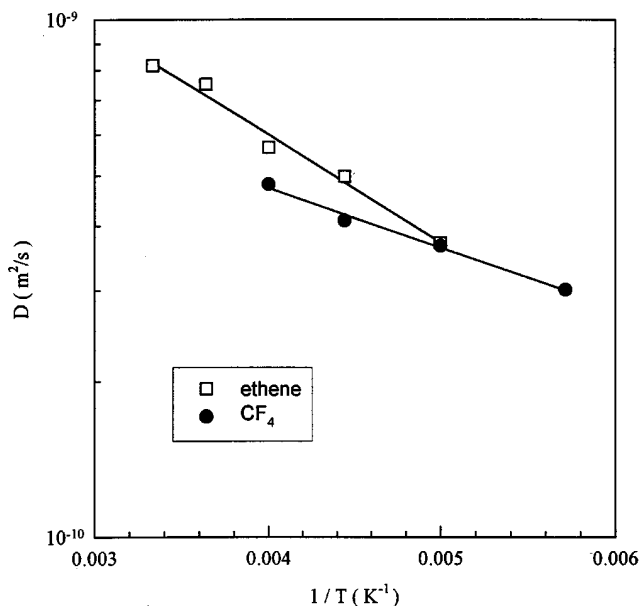
FIG. 3. Single-component self-diffusivities of ethene and CF$_4$ in silicalite at 12 molecules per unit cell.

Also shown in Fig. 3 are results for the pure-component diffusivity of the probe species CF$_4$ in silicalite. The loading is 12 molecules per unit cell. There is good agreement with previous measurements in the literature (24). CF$_4$ is seen to have a diffusivity in the same general range as the reactant ethene.

For the *in situ* diffusion studies during chemical reaction, our strategy was to use CF$_4$ as an inert probe species. ^{19}F PFG MNR was used to measure the self-diffusivity of CF$_4$ (the only species in the system containing fluorine) at various times during the conversion of ethene in H-ZSM-5. The mobility of the CF$_4$ molecules can be taken as characteristic of the mobility of other small molecules in the changing reaction system. This plan obviously requires that the CF$_4$ probe species actually is inert under these conditions. This can be easily tested by comparing the ^{19}F NMR spectra before and during the reaction. First we examined the CF$_4$ free induction decay spectra in samples where no catalytic reaction would be expected (e.g., pure CF$_4$ in silicalite or CF$_4$/ethene mixtures in silicalite). At high sorbate loadings these ^{19}F spectra displayed two peaks, which was unexpected for CF$_4$, a molecule where all fluorine atoms are equivalent. We attribute the second peak (at about 7 ppm higher field) to CF$_4$ in the gas phase, and we confirmed this by directly measuring the chemical shift of gas-phase CF$_4$. Fluorine, having a wide chemical shift range, is sensitive to the difference in environment for adsorbed species compared to those in the gas phase. Other indirect evidence supporting our peak assignment includes the following: (1) the temperature dependence of the relative sizes of the two peaks, (2) the narrow linewidth of the gas-phase peak,

and (3) identical peak positions observed for ethane/CF$_4$ mixtures and ethene/CF$_4$ mixtures. ^{19}F free induction decay spectra measured during ethene reaction at 343 K are presented in Fig. 4 for the beginning of the reaction ($t = 0$) and after 8 h. The only peaks observed are those corresponding to adsorbed CF$_4$ and gas-phase CF$_4$, indicating that CF$_4$ does not participate in the ethene reactions at these conditions. There is some change in the relative intensities of the two peaks, as the probe species redistributes between the two phases as a result of the changing hydrocarbon composition of the system. Similar ^{19}F spectra at all temperatures studied showed no reaction of the CF$_4$ probe species. It should be noted that the *echo* spectra measured in the PFG measurements exhibit only the adsorbed-phase peak.

Results of our *in situ* diffusion measurements are shown in Fig. 5. A sample of H-ZSM-5 (II) was prepared and loaded with 4 CF$_4$ and 12 ethene molecules per unit cell as described under Experimental. At time $t = 0$ the sample was taken from a refrigerator and placed in the spectrometer at 343 K. Diffusivity measurements of the CF$_4$ probe were then performed over a period of 8 h. The measurements used ^{19}F PFG NMR with the primary Hahn spin echo and an observation time Δ of 2 ms. Optimum measurement parameters were determined beforehand using similar but nonreacting systems, e.g., CF$_4$ and ethane in silicalite. The ^{19}F NMR signal was sufficiently strong that only 16 accumulations of the spin echo were used. Each diffusivity measurement could be completed in less than 15 min, which was
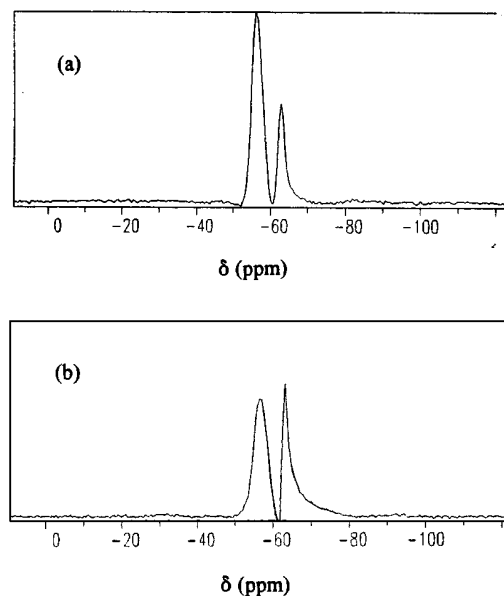

FIG. 4. ^{19}F free induction decay spectra in H-ZSM-5 (II) at 343 K. The initial compositon of the sample was 4 CF$_4$ and 12 ethene per unit cell. The first spectrum (a) was taken right after placing the sample in the spectrometer at 343 K. The second spectrum (b) was taken 8 h later. C$_6$F$_6$ (−162 ppm) (25) was used as an external chemical shift standard, and all chemical shifts are reported relative to CFCl$_3$.
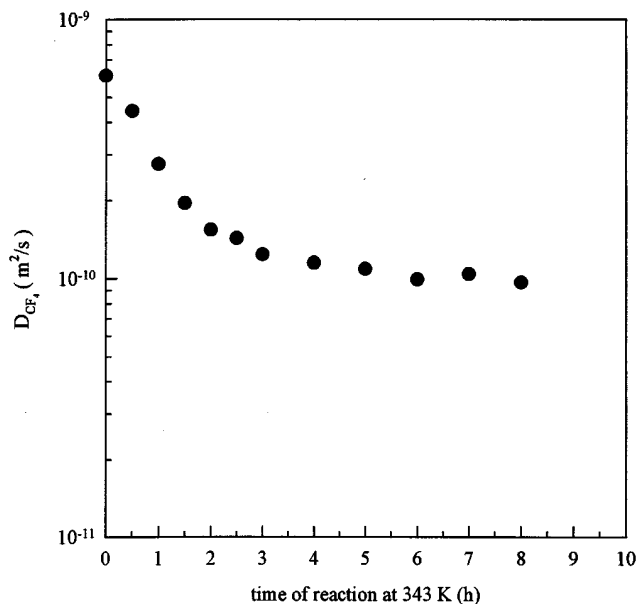
FIG. 5. Self-diffusivity of the inert CF_4 probe during ethene conversion in H-ZSM-5 (II) at 343 K. Diffusivities were measured *in situ* by ^{19}F PFG NMR during the chemical reaction. The mobility of the probe species drops by a factor of 6 during the first 3 h of reaction and then remains relatively constant.

fast enough that the system was not changing significantly during the measurement (compare Fig. 1). As the reaction proceeded and the composition of the system evolved, the CF_4 self-diffusivity fell by about a factor of 6 over the first 3 h and then was fairly constant over the next 5 h.

As the reaction proceeded, evidence of inhomogeneities in the system began to appear. This is shown in Fig. 6, which presents the echo attenuation ψ as a function of squared applied field gradient strength for various times during the reaction. Recall that from Eq. [1] the slope of such a line is proportional to the self-diffusivity. At time $t = 0$ a straight line is obtained, indicating that molecular motion over the observation time can be characterized by a single self-diffusion coefficient. As time advances, however, the figure indicates that a range of mobilities begin to appear. From the self-diffusivities and the observation time Δ, one can calculate the range of mean-squared displacements via the Einstein equation; since the mean displacements are less than the smallest zeolite crystal dimension, we can be sure that we are measuring *intra*crystalline diffusion in all cases. The self-diffusivities reported in Fig. 5 were obtained from the slopes of the lines indicated in Fig. 6. They reflect CF_4 diffusivities at the lower end of the mobility range at each point in time.

Differences in the local concentration of reaction products could produce these differences in local mobilities. There are several possible explanations for why such inhomogeneities in chemical composition might arise. With the sorbate loadings that we used, it is probable that some

ethene is in the gas phase, especially at the higher temperatures used in the reaction. We have already presented evidence of this for CF_4. If some of the ethene must diffuse to the catalytically active sites during the reaction processes, then transport limitations might give rise to inhomogeneities either across the bed of zeolite crystals or within individual crystals. The time constants for these transport processes can be estimated from knowledge of the bed dimensions and the diffusion coefficient for motion through the assemblage of crystals or from the zeolite crystal size and the diffusion coefficient within the zeolite micropores, respectively. Both of these time constants are much shorter than that for the chemical reaction, indicating that mass transport effects do not cause the observed inhomogeneities. We performed the following simple experiment to look directly for any inhomogeneity in diffusivity at different depths within the bed of crystals. For a sample that had been subjected for 8 h to reaction at 343 K we measured the echo attenuation with increasing applied field gradient strength at 300 K. Then the sample was positioned within
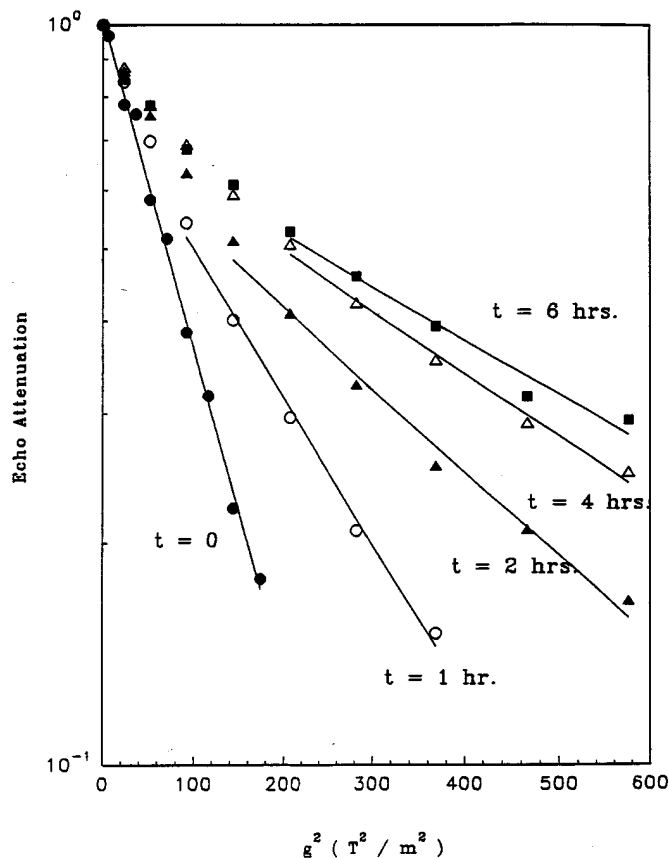

FIG. 6. Spin echo attenuation as a function of squared applied field gradient strength for the *in situ* diffusion measurements at 343 K. As time progresses, deviations from linearity indicate that mobility of the CF_4 probe can no longer be described by a single diffusivity. The lines indicate the portions of the curves from which the diffusivities in Fig. 5 were obtained.

the NMR probe such that only the lower 40% of the sample contributed to the NMR signal and the measurement was repeated. The curves of echo attenuation vs g^2 from the two measurements coincided almost exactly. This shows that the lower 40% of the sample had the same distribution of mobilities as the sample considered as a whole, supporting our view that inhomogeneities across the zeolite bed are not the cause of the range of mobilities observed. A third possibility for explaining Fig. 6 is that gradients in aluminum concentration within individual crystals could give rise to local differences in rates of reaction due to different concentrations of acid sites (26). This would result in a spatial dependence within crystals for the concentration of reaction species. Given evidence presented above against the first two possible explanations, we view the third possibility as the probable reason for the observed behavior.

The connection between the mobility of the CF_4 probe species and the chemical composition of the reacting ethene system can be seen again in Fig. 7. The CF_4 self-diffusivity is normalized by dividing by the value at $t = 0$ and is plotted versus ethene conversion. Data from Figs. 1 and 5 at 343 K are shown along with additional data at 330 K. From the studies of the ethene conversion chemistry we know that at these temperatures ethene is converted to a mix of mainly paraffinic products. These products reduce the self-diffusivity of the CF_4 probe at the reaction temperatures by almost an order of magnitude compared to the diffusivity of CF_4 in the initial CF_4/ethene mixture.

We are interested not only in the dependence of the probe mobility on conversion but also on reaction temperature. In looking at ethene conversion on H-ZSM-5, Karge et al. (6, 27) draw a distinction between low-temperature products and high-temperature products. The low-temperature products are composed largely of alkyl chains and are formed below about 500 K. The high-temperature products are composed largely of aromatics and are formed above about 500 K. Our in situ studies presented above fall into the low-temperature range, and for practical reasons it was not feasible to do in situ measurements in the high-temperature regime. Instead we heat-treated the samples in an oven and performed the diffusion measurements afterward at 300 K. Two samples were loaded with 4 molecules CF_4 and 12 molecules ethene per unit cell and sealed as described above. This was followed by treatment in an oven for 3.5 h at either 370 or 575 K. The lower temperature should be in the regime of the low-temperature products observed by Karge et al. (6), while the higher temperature should be in the high-temperature regime. Indeed, we see in Table 2 that the different chemical species formed at the two temperatures result in values of the self-diffusivitiy of the probe CF_4 at 300 K that differ by over an order of magnitude. After reaction at 370 K, we measured a range of CF_4 diffusivities of $(5–20) \times 10^{-11}$ m^2/s. After reaction at 575 K, the diffusivities are in the range $(2–3) \times 10^{-12}$ m^2/s. As in the in situ measurements, inhomogeneities arise that cause a range of molecular mobilities.

To explore further the relation between CF_4 mobility and coadsorbed hydrocarbon composition, we prepared a series of well-defined mixtures to compare against the complex compositions of the reacted samples above. These samples used the high-silica form silicalite and were stored in a refrigerator before measurements to preclude any reaction of the hydrocarbons. In all cases 4 molecules of CF_4 per unit cell were loaded with enough hydrocarbon to yield 24 carbon atoms per unit cell (12 ethene/uc, 4 hexane/uc, etc.). The self-diffusivities of CF_4 and the hydrocarbons were measured at 300 K by ^{19}F or ^{1}H PFG NMR, respectively. Ethene measurements were performed with ^{13}C PFG NMR. Results are presented in Table 3 along with some data from the literature for the pure components (28–30). The
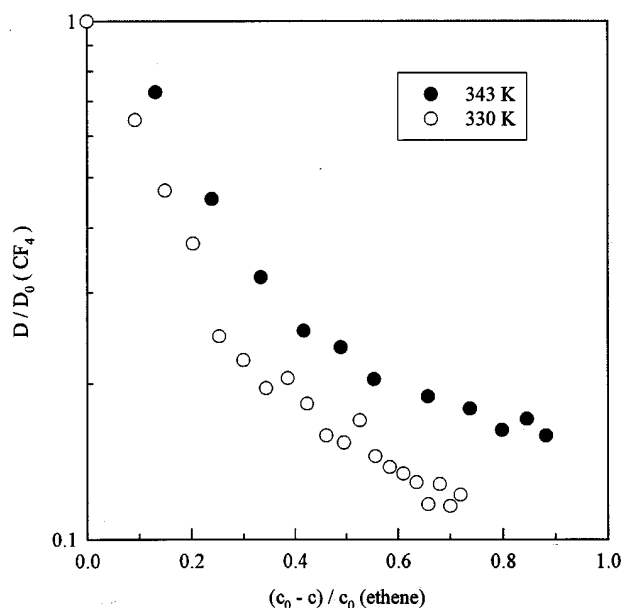

FIG. 7. *In situ* CF_4 self-diffusivity as a function of ethene conversion at 330 and 343 K. The diffusivity values are normalized by the values at $t = 0$. The diffusivity of the probe CF_4 species at reaction temperature drops almost an order of magnitude as the ethene is converted into mainly paraffinic products.

TABLE 2

Self-Diffusivities of CF_4 in m^2/s at 300 K for Samples Previously Subjected to Reaction for 3.5 h at the Temperatures Indicated

Reaction T (K)	D (CF_4)
370	$(5–20) \times 10^{-11}$
575	$(2–3) \times 10^{-12}$

Note. The samples were initially loaded with 4 CF_4/uc and 12 ethene/uc.

TABLE 3

Self-Diffusivities in m²/s at 300 K for Various Mixtures and Pure Components in Silicalite

molec/uc	D (CF_4)	molec/uc	D (hydrocarbon)
4 CF_4	2.0×10^{-9}		
4 CF_4	4.3×10^{-10}	12 Ethene	8.7×10^{-10}
4 CF_4	3.5×10^{-10}	12 Ethane	6.3×10^{-10}
4 CF_4	9.3×10^{-11}	4 Hexane	7.0×10^{-11}
4 CF_4	3×10^{-12}	4 Benzene	—
		12 Ethene	8.2×10^{-10}
		12 Ethane (28)	8.9×10^{-10}
		4 Hexane (29)	1.1×10^{-10}
		4 Benzene (30)	1×10^{-14}

Note. Each row in the table represents a single sample with either one or two adsorbed components.

self-diffusivity of CF_4 at 300 K and a loading of 4 molecules per unit cell is 2.0×10^{-9} m²/s. Upon adsorption of an additional 12 molecules per unit cell of ethene or ethane, the CF_4 diffusivity drops almost an order of magnitude. With coadsorbed hexane, it drops by more than a factor of 20, and with coadsorbed benzene the decrease is almost three orders of magnitude.

The large difference in the diffusivity of CF_4 with coadsorbed hexane or benzene (both C_6 molecules) may be due to differences in preferred adsorption siting for the hydrocarbons. From experimental evidence and molecular simulations it is thought that *n*-alkanes prefer the channel segments (31), while aromatic species adsorb preferentially in the channel intersections (32). This difference could have a significant effect on the diffusivity of the CF_4 molecules (33), since molecules in the channel intersections might block diffusion through the crystal more effectively than molecules adsorbed in the channel segments.

Based on our knowledge of the expected differences in reaction chemistry at 370 K vs 575 K, we can compare the 300 K CF_4 diffusivities after reaction of coadsorbed ethene at these temperatures (Table 2) with the results of Table 3. After reaction at 370 K, the CF_4 diffusivity is close to the CF_4 diffusivity in a nonreactive mixture with hexane in silicalite. This is consistent with our expectation that after the reaction, the CF_4 is in an environment composed largely of short alkane reaction products. Similarly, we can compare the CF_4 diffusivity after reaction at 575 K with the CF_4 diffusivity in a CF_4/benzene mixture. These two values are consistent with the fact that aromatics are the major reaction products at the higher reaction temperature.

CONCLUSIONS

In this work we have investigated the self-diffusivity of an inert probe species, CF_4, during the conversion of ethene in zeolite H-ZSM-5. As part of this work, we performed reactor studies and NMR measurements of the kinetics of ethene conversion on our zeolite samples. In agreement with previous work in the literature, we saw that at low temperatures ethene is converted mainly to paraffins and that this reaction can occur even at room temperature. The gas-phase products observed in the recirculation reactor were in the range of C_2 to C_7 alkanes at a reaction temperature of 373 K.

In the diffusion studies, the CF_4 probe molecule provides a representative example of the mobility of other small molecules in the system under changing reaction conditions. ^{19}F pulsed field gradient NMR was used to measure the self-diffusivity of the probe species during ethene conversion in H-ZSM-5. CF_4 was shown to be a suitable probe species, and its mobility was seen to be sensitive to changes in the chemical composition of the system as time progressed during the conversion of the reactant ethene. In addition, we were able to correlate CF_4 mobility in well-defined nonreacting adsorbed mixtures with the mobility and changing composition of the reacting system. Our results are consistent with data from the literature which show that at lower temperatures the main products of ethene conversion on H-ZSM-5 are paraffins while aromatics are the main products at higher temperatures. The self-diffusivity of the CF_4 probe differs by more than an order of magnitude, depending on the nature of the reaction products. The technique developed here may be useful in future studies of deactivation and coking of zeolite catalysts.

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