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In Situ Measurement of Molecular Diffusion during Catalytic Reaction by Pulsed-Field Gradient NMR Spectroscopy

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Pulsed-field gradient (PFG) NMR spectroscopy is applied to study the intracrystalline diffusivity of the reactant and product molecules during the conversion of cyclopropane to propene in Zeolite X. The diffusivities are found to be large enough that any influence of intracrystalline diffusion on the overall reaction in flow reactors may be excluded.

INTRODUCTION

There is a remarkable divergence between the high standard of the theoretical basis describing the interconnection between diffusion and reaction in heterogeneous catalysis (*1–3*) and the limited possibilities of a direct observation of the inherent processes. This is mainly due to the fact that the traditional way of analyzing molecular transport and reaction in heterogeneous catalysis is to consider the surrounding gas phase rather than the molecules in immediate contact with the catalyst.

A direct recording of the process of chemical reaction within the catalyst particles has become possible by the *in situ* application of IR (*4*, *5*) and NMR (*6–8*) spectroscopic methods. Allowing a discrimination between the various reactant, intermediate, and product molecules, these methods provide direct information about the concentration of the individual molecular species involved in the reaction within the catalyst. In Fourier transform pulsed-field gradient NMR (FT PFG NMR) (*9*) this principle of a separate recording of the individual constituents is combined with the capability of conventional PFG NMR (*10*, *11*) to determine molecular displacements within the sample. In this way the simultaneous determination of the diffusivities of the molecules involved in the process of a catalytic reaction becomes possible. The prospects and limitations of this technique as well as a first example of application are presented in this contribution.

Conditions for PFG NMR Studies during Chemical Reaction in Solid Catalysts

PFG NMR spectroscopy allows the mean square displacement $\langle r(t)^2 \rangle$ of the molecules in the interior of the catalyst particles to be determined over an observation time t of a few milliseconds and hence, via Einstein's relation,

$$\langle r(t)^2 \rangle = 6Dt, \qquad (1)$$

of the coefficient of intracrystalline self-diffusion D (*9–13*). The lower limit of the molecular root mean square displacements, observable in this way, is of the order of 1 μm, so the diameters of the catalyst particles (crystallites) must be at least of this order of magnitude to guarantee the measurement of genuine intraparticle (intracrystalline) diffusion. The definition of the self-diffusion coefficient by Eq. (1) is completely equivalent to that of Fick's first law, where D is defined as a factor of proportionality

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between the flux density of labeled molecules and their concentration gradient, when the overall concentration (i.e., the sum of the concentrations of the labeled and unlabeled molecules) is constant.

PFG NMR measurements of adsorbent–adsorbate systems are usually carried out with sealed sample tubes containing the adsorbent with a well-defined amount of adsorbed molecules under equilibrium conditions (although measurements in open systems under the conditions of molecular flow (*14*) are clearly possible, too). For multicomponent adsorption, the PFG NMR spectrum resulting from the Fourier transform of the time domain signal (the spin echo) is a superposition of the spectra of the individual components (*9, 10, 13*). Thus, provided that the spectra of the individual molecules are sufficiently different from each other, the diffusivity of any individual component may be measured. This measuring principle may be maintained if within the sample tube there is a process of molecular conversion between different species, i.e., if one has to do with nonequilibrium rather than with equilibrium conditions. The only difference is that now the molecular mobilities are studied under the influence of molecular transformations. Depending on the given state of the overall reaction, this may lead to a time dependence of the observed diffusivities.

It should be pointed out that also during the process of chemical reaction the intracrystalline concentrations of the reactant and product molecules within sealed sample tubes remain spatially constant. The measured quantities, although determined under reaction conditions, are therefore self-diffusivities. This is in contrast to the situation in conventional flow reactors where the concentrations of the individual components are space dependent and one has to do with net mass-transfer processes within the sample, being described by coefficients of transport and/or counterdiffusion. Both thermodynamic and random walk considerations (*15–17*) show, however, that at least for similar molecular species the coefficients of self-diffusion and counterdiffusion should be of the same order of magnitude.

As a consequence of the uniform distribution of the reactant and product molecules within the NMR sample tubes, molecular conversions, as observable by an inspection of the evolution of the NMR spectra, exclusively depend on the intrinsic reactivity. In contrast, any measurement of molecular conversion in flow reactors implies that reactant molecules enter and product molecules leave the catalyst particles, so for the overall process observed both the intrinsic reactivity and the transport properties of the involved molecules are of relevance.

The minimum diffusivities accessible by PFG NMR in adsorbent–adsorbate systems are of the order of 10^{-12} m^2 s^{-1} (*12, 18*). With this value and a typical maximum crystallite radius R of 50 μm, for values of the Thiele modulus

$$\varphi = R(k/D)^{1/2} \qquad (2)$$

of the order of 1 it would be necessary that the first-order intrinsic reaction-rate constants k were of the order of 4×10^{-4} s^{-1}. This means that PFG NMR diffusion studies of diffusion-controlled reactions in flow reactors (i.e., processes where the Thiele modulus is of the order of 1 or larger (*19, 20*)) necessitate intrinsic reaction-rate constants of at least this order of magnitude.

A separate determination of the diffusivities of the individual components is only possible if their spectra contain at least one line that may be easily identified within the total spectrum. The conditions to meet this requirement improve with increasing mobility of the adsorbed species (leading to smaller linewidths) and with increasing chemical shifts (leading to a larger separation between the different lines). Thus, in view of this latter criterion, the large chemical shifts of ^{13}C nuclei make ^{13}C PFG NMR a most promising tool for high-resolution diffusivity measurements during catalytic reactions. However, this advantage may be partially compensated for by the fact that the range of accessible diffusivities is smaller than in ^{1}H NMR due to the lower gyromagnetic ratio (*10, 21*).

In the present study we have measured the intrinsic molecular diffusivities during the conversion of cyclopropane to propene in Zeolite NaX using ^{1}H FT PFG NMR. The relatively high mobility of the two components and the difference between the chemical shifts of the protons in the vicinity of the double bonds and single bonds turned out to be sufficient for a separate determination of the diffusivities of the two components.

EXPERIMENTAL

We have used two specimens of Zeolite NaX with mean crystallite diameters of about 8 and 50 μm and a Si/Al ratio of about 1.2. Both specimens have been synthesized as described in Ref. (*22*). Samples were ion-exchanged three times, each time for 8 h, at 70°C with 0.1 *M* $Cd(NO_3)_2$ (*23*). The final cation exchange thus attained was 70 ± 0.5% and 72 ± 0.5% for the specimens with the large and the small crystallites, respectively. Microscopic inspection of the samples after this treatment revealed no changes in the crystal habit.

The catalytic activity of the thus-prepared zeolite samples was tested in a conventional flow reactor where 100 mg zeolite, mixed with 400 mg quartz (with a grain size of 0.2–0.4 mm), was spread over a frit of 8 mm diameter with a bed height of 15 mm. The catalysts were activated in a stream of pure, dry helium at a flow rate of 2 liters h^{-1} by increasing the temperature over 3 h up to 200°C. The samples were kept at the final temperature for 2 h. The reaction was studied within a stream of dry helium gas, containing 2.5 vol% of cyclopropane at the same flow rate and temperature. The conversion of cyclopropane to propene was determined by gas chromatographic analysis of the reactor effluent. The temperature could be adjusted with an accuracy of ±1 K.

The FT PFG NMR self-diffusion measurements have been carried out by means of a homebuilt spectrometer (UDRIS) at a proton resonance frequency of 90 MHz. The pulse widths of the magnetic field gradient were varied between 0 and 0.7 ms with a maximum gradient intensity of 4 T m^{-1}. For the measurements, the pulse sequence of the primary spin echo ($\pi/2$–τ–π–τ–spin echo) (*9–13*) with accumulation numbers typically of 100 was applied. The mean error in the obtained diffusivities was of the order of 30% maximum (*12*). Values of the intracrystalline mean lifetime of cyclopropane have been determined by the NMR tracer desorption technique (*12*) using the stimulated echo ($\pi/2$–τ_1–$\pi/2$–τ_2–$\pi/2$–τ_1–echo) (*10*). The spectra obtained by Fourier transform of the free induction decay following the $\pi/2$ pulse were used for the determination of the concentrations of cyclopropane and propene within the sample. Hence, by analyzing the time dependence of these concentrations, the intrinsic reaction rates in addition to the diffusivities could be determined.

RESULTS

Conversion of Cyclopropane to Propene in NaCdX: Macroscopic Experiments

The conversion of cyclopropane to propene in X-type zeolites in a micropulse flow reactor has been extensively studied by Benn *et al.* (*24*) and Abbas *et al.* (*25*). It was found that the activity significantly depends on the cations. In contrast to the relatively inactive alkali forms of X-type zeolites, the ion exchange of transition metal ions, e.g., Co^{2+} and Mn^{2+}, leads to an increase of the reaction rates in dependence on the level of ion exchange. Moreover, it was found that the activation energy of the reaction is relatively independent of the level of ion exchange (*24*). An additional enhancement of the activity was observed when the sample activation was carried out at moderate temperatures (about 473 K) (*26, 27*). In this case, via Plank's mechanism, residual water molecules lead to the formation of additional OH groups (*28*). In our measurements we have used NaCdX, taking advantage of the nonparamagnetic character of the Cd^{2+} ion, since the presence of paramagnetic ions would have led to a further reduction of the nuclear magnetic relaxation times and hence to a substantial limitation of the applicability of PFG NMR.

We have tested the activity for the two specimens of NaCdX in a flow reactor at 473 K under reaction conditions identical to those described above. The apparent first-order reaction-rate constants k_{app} derived from the conversion of cyclopropane, the catalyst weight, and the flow rate, are 4.0×10^{-5} and 4.8×10^{-5} mol $\mathrm{g}_{\mathrm{cat}}^{-1}$ s^{-1} atm^{-1} for the large- and small-crystallite sample, respectively. Assuming a reaction-limited process the intrinsic reaction rate constants k_{intr} were determined via the relation

$$k_{\mathrm{intr}} = k_{\mathrm{app}}/K_{\mathrm{ads}}, \qquad (3)$$

where $K_{\mathrm{ads}} = n_{\mathrm{ads}}/p_{\mathrm{cyclopropane}}$ is the adsorption constant with n_{ads} and $p_{\mathrm{cyclopropane}}$ denoting the mole number of adsorbed cyclopropane per gram catalyst and the partial pressure of cyclopropane, respectively. By extrapolation from the adsorption isotherms determined between 298 and 353 K to the reaction temperature of 473 K the value of K_{ads} was estimated to be $(1.9 \pm 0.2) \times 10^{-2}$ mol $\mathrm{g}_{\mathrm{cat}}^{-1}$ atm^{-1}. Inserting this value into Eq. (3) yields intrinsic rate constants of 2.1×10^{-3} and 2.5×10^{-3} s^{-1} for the large- and small-crystallite sample, respectively. Since the slight difference in the reactivities for the two crystallite sizes may be easily attributed to a difference in the cation contents, the reactivity may be considered to the independent of the crystallite size, suggesting that the overall reaction rate is unaffected by intracrystalline diffusion.

PFG NMR Measurement of Single-Component Self-Diffusion

Figures 1a and 1b show the concentration and temperature dependence of the coefficients of self-diffusion of cyclopropane and propene in Zeolites NaX and NaCdX. The measurements have been carried out with dehydrated samples over a time interval sufficiently short that no conversion took place. In agreement with previous studies (*12*), the unsaturated hydrocarbons were found to be less mobile than the saturated hydrocarbons, although the difference in the mobilities (factor 1.5–2) is less than that observed in other cases as, e.g., for ethane and ethene in NaX where the difference is nearly one order of magnitude (*12*). The mobility decreases with increasing concentration (concentration dependence of type I/II (*12*)), which may be considered a mutual hindrance to the molecules. The activation energies determined from the temperature dependence of the intracrystalline diffusivities of cyclopropane and propene (Fig. 1b) are 9.8 ± 1 and 11.2 ± 1 kJ/mol, respectively, in NaCdX and 9.2 ± 1 and 10.7 ± 1 kJ/mol, respectively, in NaX.

The PFG NMR measurements have been carried out with the sample of larger crystallites. However, test experiments with the smaller crystallites revealed no differences in the obtained diffusivities as expected as long as the observed molecular mean square displacements are smaller than the mean crystallite radii (*12*).

PFG NMR Two-Component Self-Diffusion Measurements

In NaCdX, the linewidths of the ^{1}H NMR signals of cyclopropane and propene turned out to be too large to separate the contributions of the two sepecies of the ^{1}H NMR spectrum. In our two-component self-diffusion measurements we were confined therefore to NaX. As an example, Fig. 2 shows the ^{1}H NMR spectrum of a 1 : 1 mixture of cyclopropane and propene adsorbed in NaX at a total concentration of two molecules per cavity, resulting from the Fourier transform of the spin echo and its dependence on the width of the applied-field gradient pulses. The larger peak at a chemical shift $\delta = 0$ ppm is due to the protons of cyclopropane and of the $-\mathrm{CH}_3$ group of propene, while the smaller peak at $\delta = 4$ ppm stems from the protons of the $-\mathrm{CH{=}CH}_2$ group. If the attenuation of the spin echo due to nuclear magnetic relaxation is either negligibly small or

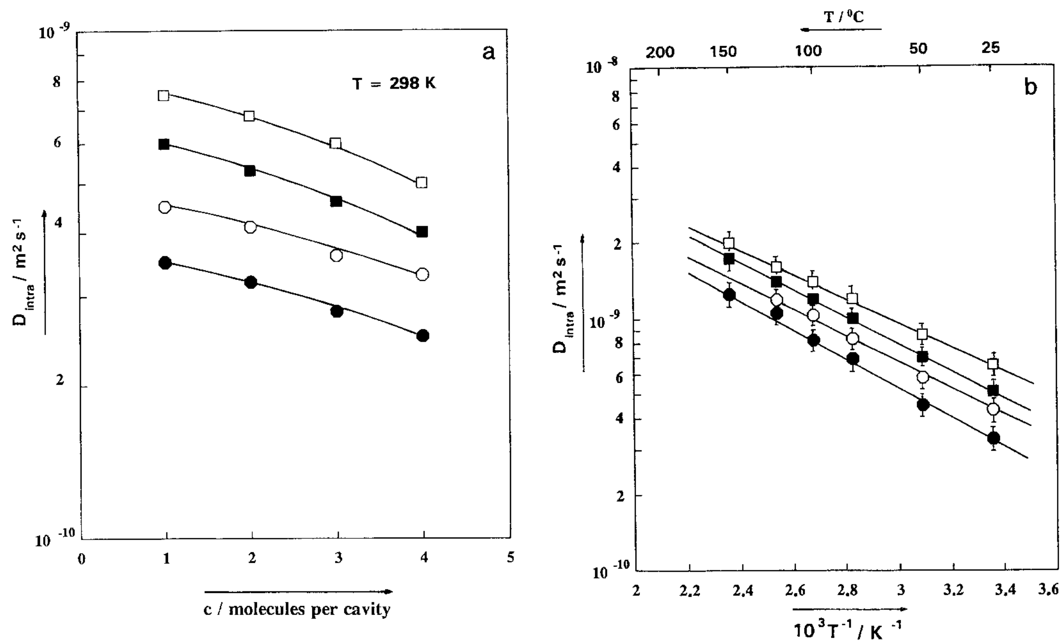

FIG. 1. Self-diffusion coefficients of cyclopropane (□, ■) and propene (○, ●) adsorbed in NaX (open symbols) and NaCdX (solid symbols). (a) Concentration dependence at 298 K, (b) temperature dependence at a sorbate concentration of two molecules per cavity.

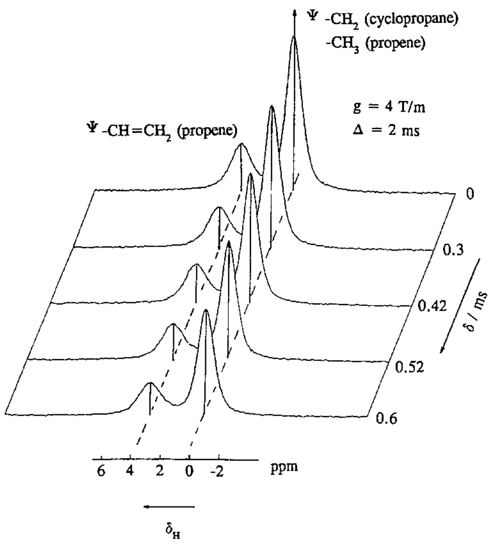

FIG. 2. ^{1}H PFG FT NMR spectra of a 1 : 1 mixture of cyclopropane and propene adsorbed in NaX at a total concentration of two molecules per cavity at 298 K for increasing values of the field gradient pulse width δ. The pulse separation (Δ) and the intensity of the field gradient pulses g are 2 ms and 4 T m^{-1}, respectively.

similar for both components, in the spectrum observed without field gradients, the intensity of the two lines must be proportional to the number of protons contributing to them. The quantitative analysis yields a ratio of 3 : 1, which is in agreement with the expected behavior.

Figure 3 shows the diffusivities of cyclopropane and propene for two-component adsorption in NaX at a total sorbate concentration of two molecules per cavity for various compositions, determined from the attenuation of the ^{1}H NMR NMR spectra with increasing pulsed-field gradient duration. It turns out that despite the different mobilities for single-component adsorption, in the mixture the mobilities of the two components are essentially the same. This experimental finding is in agreement with previous PFG NMR studies performed on the neat liquids (*13*) and on adsorbent–adsorbate systems (*9*) where the differences in the mobilities of the individual components within a mixture were found to be much less than in the pure components. Again, under the

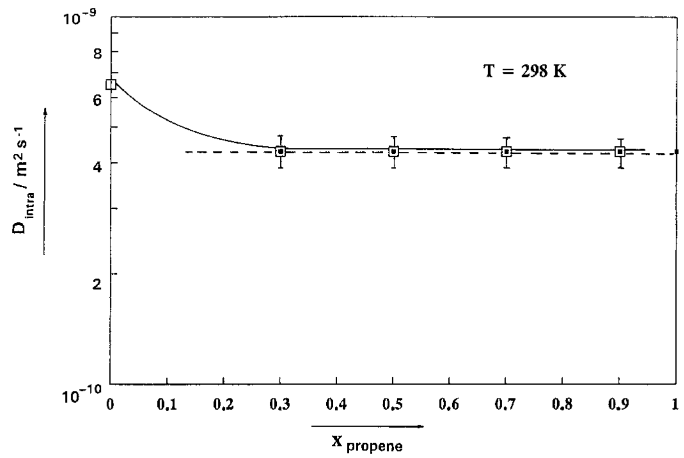

FIG. 3. Self-diffusion coefficients of cyclopropane (□) and propene (■) for two-component adsorption in NaX at a total sorbate concentration of two molecules per cavity for various compositions, determined by ^1H PFG FT NMR measurements at 298 K.

chosen measuring conditions (298 K, no residual water) any intrinsic reaction during the time of measurement could be excluded.

It is noteworthy that in the given case the coefficients of self-diffusion are identical for both components and, moreover, remain constant with varying composition. In such a case (cf., e.g., Refs. (*12*, *15–17*, *19*)) the self-diffusivities of both components may in fact be expected to coincide with the coefficient of counterdiffusion.

PFG NMR Diffusion Measurements during Catalytic Reaction

In order to make the reaction as fast as possible, the measurements have been carried out with a zeolite NaX specimen activated at only 473 K under vacuum (final pressure $p = 5 \times 10^{-3}$ Pa), so that about one water molecule per cavity remained within the zeolite crystallites (*29*). The measurements have been carried out in a temperature range 453 to 483 K, the highest temperature presently accessible for the PFG NMR spectrometer in use. Figure 4 shows the time dependence of the concentration of the two molecular species and their diffusivities. It turns out that the measured diffusivities are of the order to magnitude one would expect by extrapolating from the measurements outside the reaction conditions (Figs. 1 and 3). In particular, for the given system during the whole process

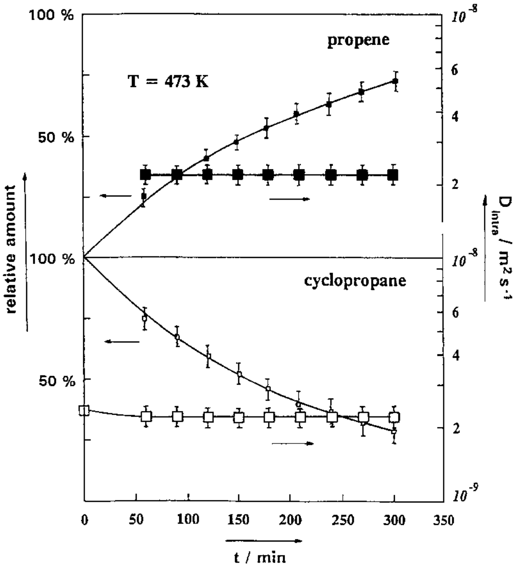

FIG. 4. Time dependence of the relative amount of cyclopropane and propene during the conversion of cyclopropane to propene in NaX and their self-diffusion coefficients (□, cyclopropane; ■, propene) at 473 K.

TABLE 1

Comparison of the Values of the Intracrystalline Mean Lifetime (τ_{intra}) of Cyclopropane in Various X-Type Zeolites with the Theoretical Values ($\tau_{\text{intra}}^{\text{diff}}$) Determined from Eq. (4)

Zeolite	R (μm)	T (K)	D_{intra} ($\text{m}^2\ \text{s}^{-1}$)	$\tau_{\text{intra}}^{\text{diff}}$ (Eq. (4)) (ms)	τ_{intra} (ms)
NaX	25	373	1.5×10^{-9}	27	28
NaCdX	25	373	1.1×10^{-9}	38	40
NaCdX	4	253	2×10^{-10}	5	6

of conversion the diffusivities of both the reactant and the product molecules are found to be essentially identical and constant.

Via the relation

$$\tau_{\text{intra}}^{\text{diff}} = R^2/(15\,D_{\text{intra}}), \quad (4)$$

with R^2 denoting the mean square crystallite radius, the measured diffusivities may be used to determine the mean lifetime ($\tau_{\text{intra}}^{\text{diff}}$) of the reactant and product molecules within the individual crystallites, assuming that the molecular exchange is exclusively controlled by intracrystalline diffusion (*12*). It is shown in Table 1 that these values agree well with the real intracrystalline mean lifetime τ_{intra} directly determined by ^{1}H NMR tracer-desorption studies of single-component systems. Any influence of an additional transport resistance on the outer surface of the crystallites (surface barriers) may therefore be excluded.

The values of $\tau_{\text{intra}}^{\text{diff}}$ must be compared with the mean intrinsic reaction time τ_{reaction}, which is related to the intrinsic rate constant by

$$\tau_{\text{reaction}} = 1/k_{\text{intr}}. \quad (5)$$

For $\tau_{\text{intra}} \ll \tau_{\text{reaction}}$, any limitation of the overall reaction by intracrystalline diffusion which corresponds with a Thiele modulus (see Eq. (2)) much less than 1 may be excluded.

Table 2 provides a summary of the values of the intrinsic reaction rate constant for the conversion of cyclopropane to propene in various X-type zeolites. The reaction times following from them via Eq. (5) are five to six orders larger than the intracrystalline molecular mean lifetime under the given experimental conditions. Hence, in agreement with the fact that the reaction rates observed in the flow reactor are independent of the crystal size, any influence of intracrystalline diffusion on the conversion rate of cyclopropane to propene may be excluded.

Figure 5a shows the relative amount of cyclopropane during the conversion to pro-

TABLE 2

Intrinsic Reaction-Rate Constants for the Conversion of Cyclopropane to Propene in Various X-Type Zeolites at 473 K

Zeolite	$10^4\ k_{\text{intrinsic}}$ (s^{-1})	Mode of measurement	Reference
NaX	5.1	Micropulse flow reactor	(*24*)
NaX	1.7	Micropulse flow reactor	(*30*)
NaCdX	25	Flow reactor	This paper
NaX	0.7	NMR *in situ*	This paper

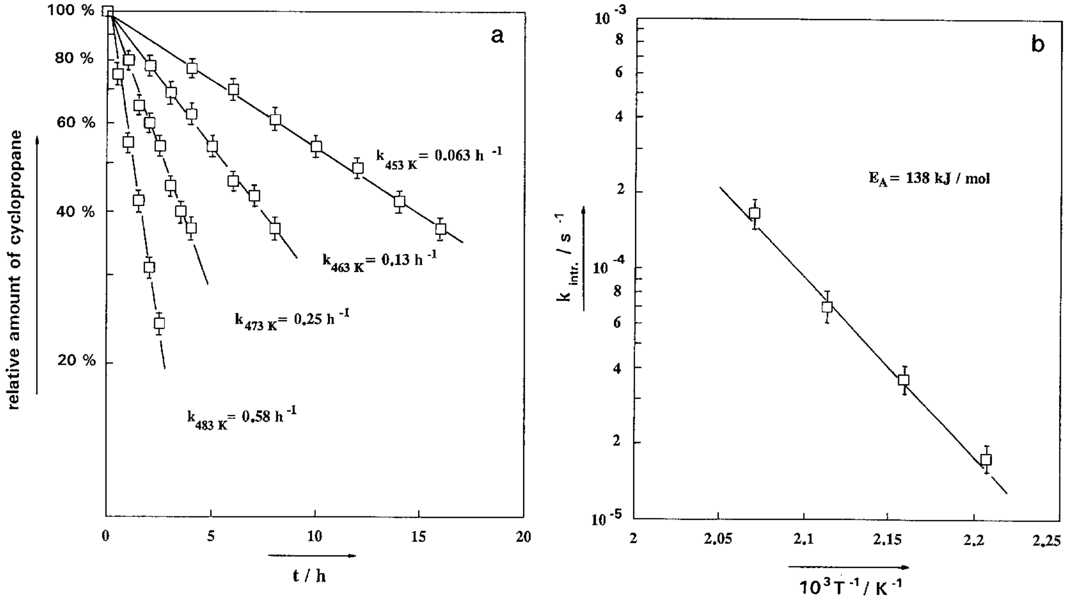

FIG. 5. The relative amount of cyclopropane during the conversion of cyclopropane to propene in NaX as determined from the ^{1}H NMR spectra in dependence on the reaction time and the Arrhenius plot of the obtained first-order intrinsic reaction-rate constants.

pene as determined from the ^{1}H NMR spectra in dependence on the reaction time at four different temperatures. In all cases the time dependence of a first-order reaction is observed. The absolute values of both the reaction rate constants (Fig. 5b) and their activation energies (138 ± 14 kJ mol^{-1}), the latter being more than one order of magnitude larger than the values for the activation energy of the intracrystalline diffusion (cf. Fig. 1b), are of the same order as literature data reported for flow reactor measurements (*24*, *30*) (see Table 2). This agreement again confirms that for the given system any influence of molecular diffusion on the measurements with the flow reactors may be excluded.

CONCLUSIONS

1. PFG NMR spectroscopy has been demonstrated to permit the *in situ* determination of the diffusivities of the individual reactant and product molecules during catalytic reactions.
2. In the case of conversion of cyclopropane to propene over X-type zeolites, the diffusivities under reaction conditions may be estimated by extrapolation from the diffusivities determined under conditions where the conversion rates are still negligibly small. The diffusivities of the reactant and product molecules are found to remain essentially constant during the process of conversion. The measured diffusivities are so high that any influence of intracrystalline diffusion on the overall process in flow reactors may be excluded.
3. As a consequence of the small chemical shifts and the large linewidths, the possibilities of ^{1}H PFG NMR for selective multicomponent self-diffusion measurements during catalytic reactions are limited. Better prospects will be provided by ^{13}C PFG NMR.

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