JOURNAL OF CATALYSIS **167,** 248–255 (1997)
ARTICLE NO. CA971544

In Situ ^{13}C Fourier Transform Pulsed Field Gradient NMR Study of Intracrystalline Diffusion during Isopropanol Conversion in X-Type Zeolites

H. B. Schwarz,* S. Ernst,† J. Kärger,*,[1] B. Knorr,* G. Seiffert,* R. Q. Snurr,‡ B. Staudte,* and J. Weitkamp†

**Fakultät für Physik und Geowissenschaften, Universität Leipzig, D-04103 Leipzig, Federal Republic of Germany; †Institut für Technische Chemie I,*
Universität Stuttgart, D-70569 Stuttgart, Federal Republic of Germany; and ‡Department of Chemical Engineering,
Northwestern University, Evanston, Illinois 60208

Received September 20, 1996; revised November 18, 1996; accepted November 18, 1996

^{13}C Fourier transform pulsed field gradient NMR was applied for the first time for the *in situ* observation of the self-diffusion of reactant and product molecules during a zeolite-catalyzed reaction. The conversion of isopropanol in LiNaX-51, NaX, CsNaX-60, and CsNaX-60 · 8CsOH either to acetone, as the product of base catalysis, or to propene, as the product of acid catalysis, was chosen as a model reaction. In NaX and CsNaX-60, the self-diffusivities of isopropanol and propene were shown to depend explicitly on the reaction time. In the considered cases any limitation of the overall reaction by intracrystalline diffusion could be excluded. It was found that, in CsNaX-60 · 8CsOH, the isopropanol conversion probably follows the base-catalyzed reaction pathway, while in the other cases formation of propene is indicative of a substantial contribution of acid catalysis. © 1997 Academic Press

INTRODUCTION

Over the past 30 years many studies have been devoted to the acid properties of zeolites because of their important applications in catalysis, especially in petroleum refining. By contrast, the use of zeolites as basis catalysts is an underdeveloped area (1, 2). Basic zeolites are attractive microporous materials for both economic and environmental reasons (3), since they replace corrosive liquid bases in chemical plants and eliminate the problems associated with their disposal.

In zeolites, the presence of basic sites was first shown in the alkylation of toluene with methanol on alkali metal cation exchanged faujasites (4–11). The nature of these basic sites was further investigated in detail and related to the framework oxygen atoms (5). A clear influence of the framework oxygen basicity was observed in the transformation of isopropanol on X- and Y-type zeolites exchanged with different alkali metal cations (12, 13). Isopropanol is dehydrated to propene on acid catalysts. With decreasing acidity of the catalyst (density and/or strength of acid sites) dehydrogenation of isopropanol to acetone becomes increasingly important. Many other examples of acid–base catalysis in zeolites are described elsewhere (14–21).

A variety of other catalytic reactions have been proposed for testing the basic versus the acidic and basic properties of zeolites. Huang and Kaliaguine describe the reaction of methylbutynol on alkali-exchanged zeolites (22) and the vapor-phase reaction of methanol with acetone (16). Berkani *et al.* investigated the transformation of cyclopentanol in the presence of cyclohexanone (23), while Burger (24) studied the reaction of acetonylacetone. The catalytic transformations in the "dimethylamine–formaldehyde–water" system were described by Romannikov (25). In all these reactions the yield of the corresponding products has been claimed to reveal the acidic or basic properties of oxide catalysts. Beside catalytic test reactions, the O1s bonding energies obtained from X-ray photoelectron spectroscopy may be used as another measure of the basicity of zeolites (26, 27). This method was applied to zeolites by Grünert *et al.* (28).

In zeolite catalysis mass transfer may play a decisive role (29, 30). Diffusional effects may contribute to the observed reaction rate, selectivity, or both. Understanding diffusion in zeolites is therefore crucial for the development of processes using zeolite catalysts. Nevertheless, direct *in situ* measurements of diffusion under reaction conditions are nearly nonexistent in the literature. Hong *et al.* (31) demonstrated that proton Fourier transform pulsed field gradient (FT PFG) NMR spectroscopy allows, under certain conditions, the direct measurement of the self-diffusivities of the individual reactant and product species during catalytic reactions. They applied this technique to the investigation of the conversion of cyclopropane to propene in NaX. The self-diffusivities of both molecules were simultaneously determined as a function of conversion as the reaction proceeded. For this system, the self-diffusivities of the reactant

---

[1] To whom correspondence should be addressed. Fax: +49-341-9732549. E-mail: Kaerger@server1.rz.uni-leipzig.de.

0021-9517/97 $25.00

and product species were found to be essentially the same, and they remained constant during the course of the reaction. As a consequence of the small chemical shifts and the large linewidths, the possibilities of the ^{1}H FT PFG NMR technique for selective multicomponent self-diffusion measurements during catalytic reactions are limited. Hong *et al.* (31) proposed the use of ^{13}C FT PFG NMR, because of its larger chemical shifts. The experimental conditions for this method are the same as for those in the *in situ* ^{1}H FT PFG NMR technique.

^{13}C nuclear magnetic resonance is a well-established technique in zeolite catalysis (32–40). The advantage of this method is the possibility to study highly reactive adsorbates on catalysts in considerable detail. Beside this, one may be able to look at the sequence of reaction steps that occur after the adsorption of molecules on zeolites.

Snurr *et al.* (41) reported ^{19}F PFG NMR measurements of the self-diffusivity of tetrafluoromethane (CF_4) during the conversion of ethene in H-ZSM-5. CF_4 did not participate in the reaction but served as an inert probe species, whose mobility could be considered to be representative for that of small molecules in the system. This approach, however, did not provide a direct measurement of reactant and product diffusivities as described by Hong *et al.* (31).

In the present study, *in situ* ^{13}C Fourier transform pulsed field gradient NMR was applied for the first time to study the self-diffusivities of reactant and product molecules during a catalytic reaction. As a model reaction, the conversion of isopropanol either to propene or to acetone in X-type zeolites was chosen.

EXPERIMENTAL

Zeolite NaX with a silicon-to-aluminium ratio of 1.3 and a crystallite size in the range from 10 to 30 μm was synthesized according to the method of Charnell (42). After excessive ion exchange of this material with an aqueous solution of cesium chloride at 353 K, 60% of the initially present sodium ions was replaced by cesium ions. The resulting material was denoted as CsNaX-60. This zeolite was further impregnated with an aqueous solution of $CsOH \cdot H_2O$ such as to achieve a loading of eight molecules CsOH per unit cell. This zeolite was designated as CsNaX-60 · 8CsOH. Furthermore, NaX was excessively ion exchanged with an aqueous solution of lithium chloride at ambient temperature. The degree of ion exchange of the resulting zeolite amounted to 51% of the initially present sodium ions. This zeolite, denoted as LiNaX-51, was synthesized in an endeavor to achieve higher catalytic activity, thus enabling reaction temperatures below the 473 K, i.e., the maximum temperature applicable in our PFG NMR spectrometer (43).

Samples for the NMR measurements were prepared by heating 9-mm-high layers of zeolites in glass tubes of 8 mm diameter. The temperature was increased at a rate of 10 K h^{-1} under vacuum. After maintaining the samples at 673 K and at a pressure lower than 0.01 Pa for 24 h, the samples were loaded with a known amount of adsorbate and sealed off. For the characterization of LiNaX-51 the intracrystalline self-diffusivities of propane (>99.5%, Merck Schuchardt, Hohenbrunn, Germany), propene (>98%, Fluka Chemie AG, Basel, Switzerland), isopropanol (>99.5%, Fluka Chemie AG, Basel, Switzerland), and acetone (>99.5%, Fluka Chemie AG, Basel, Switzerland) were measured by proton pulsed field gradient NMR, which is described in detail in (29). The concentration of these adsorbates amounted to 16 molecules per unit cell in the case of propane and 24 molecules per unit cell in all other cases.

The reaction of isopropanol in LiNaX-51, NaX, CsNaX-60, and CsNaX-60 · 8CsOH was followed by ^{13}C-NMR. After activation of the zeolites as described above, the four zeolites were loaded with 24 molecules of isopropanol-2-$^{13}C_1$ (>99 atom% ^{13}C, IC Chemikalien, Ismaning, Germany) per unit cell. To ensure that the diffusion measurements can be carried out under well-defined conditions, the time of measurement must be kept sufficiently small in comparison with the time of reaction. Therefore, in a first step, a suitable reaction temperature had to be found by investigating the conversion kinetics of isopropanol.

These preliminary investigations and the *in situ* ^{13}C FT PFG NMR self-diffusion measurements were carried out on the home-built spectrometer Fegris 400 (43) at a resonance frequency of $\nu(^{13}C) = 100.63$ MHz. For the investigation of reaction kinetics several NMR samples were tempered at various temperatures over different time intervals. After cooling to ambient temperature, single-pulse excitations (Bloch decays) were performed at ambient temperature with a repetition time of 20 s and a $\pi/2$-pulse length of 14.5 μs. In view of ^{13}C T_1 values of the order of 4 s this repetition time proved to be large enough to ensure an unbiased spectra accumulation. All spectra were Bloch decay spectra obtained by Fourier transformation of the free induction decays. One-hundred eighty transients were averaged so that the signal-to-noise ratio was sufficient to allow measurements of the chemical shifts within an uncertainty of 0.1 ppm. [$^{13}C_6$] Benzene (128.5 ppm) was used as an external chemical shift standard, and all shifts are reported relative to tetramethylsilane. The intensity of the signals in the ^{13}C-NMR spectra were used for the determination of the concentration of isopropanol and propene/acetone within the sample as a function of reaction time. Hence, the temperature dependence of the intrinsic reaction rate constants could be determined.

During all *in situ* ^{13}C FT PFG NMR measurements, a free induction decay was first performed in order to confirm the conversion rate of isopropanol as a function of reaction time. Thereafter, the pulse sequence of the primary spin echo ($\pi/2$-τ-π-τ-spin echo) (29, 44) with a fixed pulse duration of $\delta = 2.2$ ms and a fixed observation time for diffusion Δ with $\Delta = 4$ ms was applied. Each diffusion measurement was performed by varying the gradient amplitude g from 0 to 24 $\mathrm{T \cdot m^{-1}}$. Given the repetition time and the number of accumulation needed, the duration of such an *in situ* ^{13}C FT PFG NMR measurement amounts nearly to 15 h. Between two subsequent *in situ* ^{13}C FT PFG NMR measurements each NMR probe was tempered for a time interval between 10 and 15 h in an oven at the reaction temperatures. After this procedure the samples were stored in a refrigerator until the next ^{13}C FT PFG NMR measurement in order to avoid uncontrolled further reactions. The spectra obtained by Fourier transformation of the primary spin echo were used for the separate determination of the self-diffusivities of the reactant and product molecules. These self-diffusivities D were obtained from the attenuation of the area of the signal $\Psi(\delta g, \Delta)$ with increasing amplitude g of the pulsed field gradients

$$\Psi(\delta g, \Delta) = \exp[-\gamma^2 \delta^2 g^2 D(\Delta - \delta/3)], \qquad [1]$$

where γ is the gyromagnetic ratio of the necleus under observation (29).

RESULTS AND DISCUSSION

Characterization of LiNaX-51

Figure 1 presents the Arrhenius plots of the intracrystalline diffusion coefficients of acetone, isopropanol, and propene in LiNaX-51. Within the accuracy of the measurements, the intracrystalline self-diffusion coefficients of acetone and isopropanol are equal. The diffusivity of propene is seen to be remarkably larger than that of isopropanol or acetone. This trend in the diffusivities was also observed in NaX, CsNaX-60, and CsNaX-60 · 8CsOH (45). If the acid and base catalyzed reactions occurred in parallel, the faster diffusion of propene could favor the macroscopically observable production of this species in the case that the process is diffusion limited.

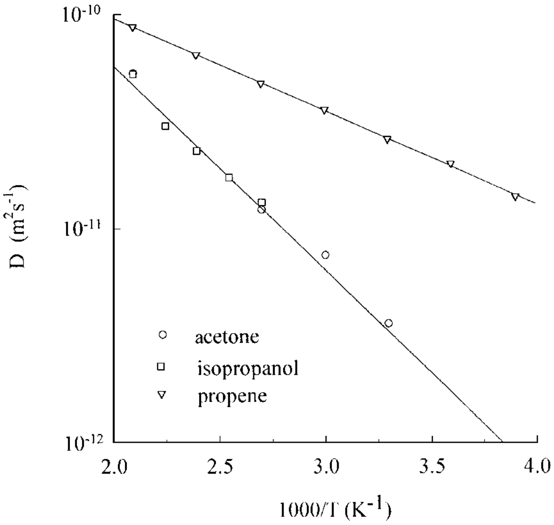

FIG. 1. Intracrystalline diffusion coefficients of acetone, isopropanol, and propene in LiNaX-51.

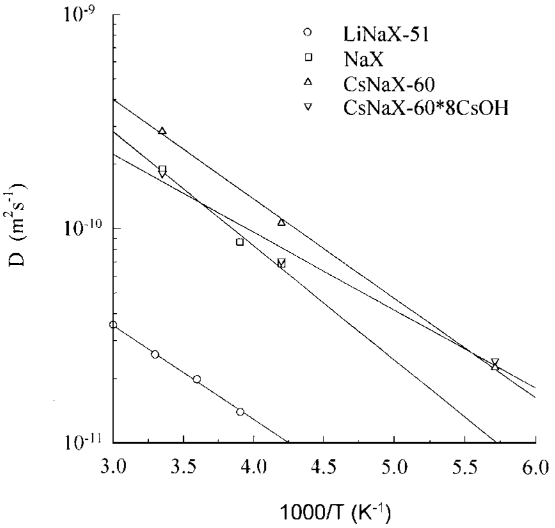

FIG. 2. Intracrystalline diffusion coefficients of propene in LiNaX-51, NaX, CsNaX-60, and CsNaX-60 · 8CsOH.

Figure 2 presents a comparison of the intracrystalline diffusivities of propene in all four X-type zeolites. Considering only the nonimpregnated zeolites (LiNaX-51, NaX, and CsNaX-60) an increasing self-diffusivity of propene with increasing size of the cations is observable. This may be explained by the specific interaction of the π-electron-cloud of propene with the empty valence orbital of the cations in the supercages of the zeolites. This explanation is confirmed by complementary diffusion studies with propane. The molecular volume of propane is comparable to that of the reactant and product molecules under study, but it is expected to undergo no specific interactions with the cations nor with the zeolitic framework. Correspondingly, the intracrystalline self-diffusion coefficients of propane increase with decreasing size of the cations $\mathrm{Cs^+}$ (D(300 K) $\sim 2.7 \times 10^{-10}$ $\mathrm{m^2\,s^{-1}}$), $\mathrm{Na^+}$ (D(300 K) $\sim 7.1 \times 10^{-10}$ $\mathrm{m^2\,s^{-1}}$), and $\mathrm{Li^+}$ (D(300 K) $\sim$ 2.4×10^{-9} $\mathrm{m^2\,s^{-1}}$). The lower diffusivities of propene in the impregnated zeolite CsNaX-60 · 8CsOH in comparison with CsNaX-60 may be explained by steric hindrance due to the existence of cesium oxide or hydroxide particles in the supercages of CsNaX-60.

Table 1 presents the activation energies E_a and the pre-exponential factors D_0 of the diffusivities for the molecules under consideration in LiNaX-51 resulting from the evaluation of the Arrhenius plots.

Preliminary Investigation of the Reaction Behaviour of Isopropanol

It is well known (29, 46, 47) that the diffusivity of molecules depends on their concentration. In order to

TABLE 1

Results from the Evaluation of the Arrhenius Plots

Zeolite	Adsorbate	E_a (kJ mol^{-1})	D_0 (m^2 s^{-1})
LiNaX-51	Acetone	18.1 ± 0.8	$(4.8 \pm 1.2) \times 10^{-9}$
	Isopropanol	18.4 ± 1.8	$(4.9 \pm 2.5) \times 10^{-9}$
	Propane	9.1 ± 0.4	$(9.1 \pm 1.1) \times 10^{-8}$
	Propene	8.4 ± 0.1	$(7.2 \pm 0.2) \times 10^{-10}$

Note. E_a, activation energy; D_0, preexponential factor.

determine the intracrystalline self-diffusion coefficients of the reactants during chemical reaction under well-defined conditions, a reaction temperature must therefore be chosen at which the change in the concentration during the time of measurement is negligibly small. On the other hand, the temperature cannot be chosen too small since in this case too large reaction times would become necessary. In order to find a suitable reaction temperature for the *in situ* ^{13}C FT PFG NMR measurements, the conversion of isopropanol at various temperatures was monitored in a preliminary study by recording the ^{13}C-NMR spectra as a function of the reaction time. As an example, Fig. 3 shows a typical plot of the ^{13}C-NMR spectra of [$^{13}C_1$]2-isopropanol in NaX at a reaction temperature of 541 K, as following from transformation of the free induction decays. In each spectrum two peaks appear. The peak at a chemical shift $\delta_1 = 63.1$ ppm is due to [$^{13}C_1$]2-isopropanol (48), while the peak at $\delta_2 = 139.9$ ppm is due to [$^{13}C_1$]2-propene (48).

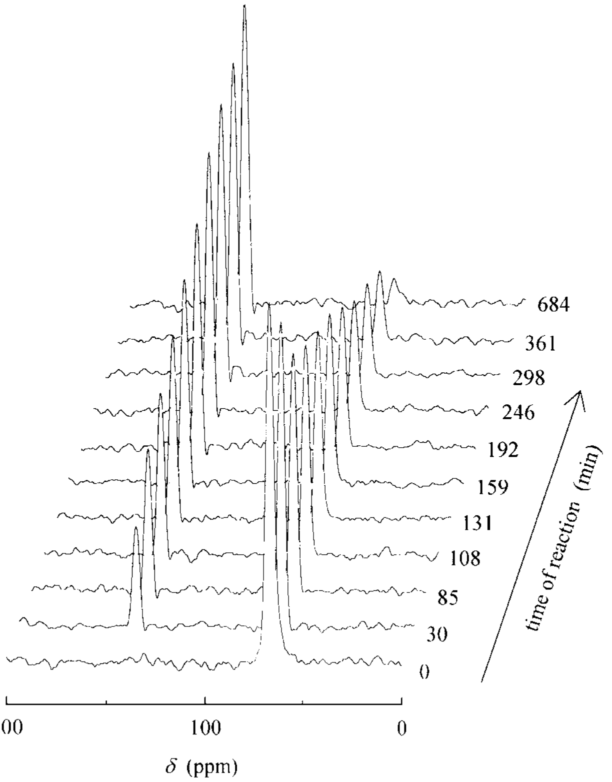

FIG. 3. ^{13}C FT NMR spectra of [$^{13}C_1$]2-isopropanol in NaX at 541 K as a function of the reaction time.

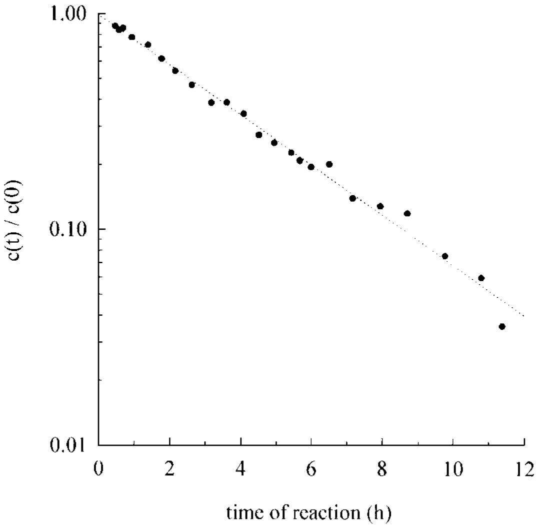

FIG. 4. Semilogarithmic plot of the relative concentration of [$^{13}C_1$] 2-isopropanol in NaX at 541 K as a function of the reaction time.

Figure 4 shows the relative concentration of isopropanol (i.e., the intensity of the line at 63.1 ppm in Fig. 3) in a semilogarithmic representation against the reaction time. As expected, the catalytic conversion of isopropanol to propene is found to be a first-order reaction. The estimated reaction rate constant is approximately 8×10^{-5} s^{-1}. Similar investigations with the other X-type zeolites yielded the following sequence in the reaction rates of isopropanol conversion at 473 K:

$$r(\text{LiNaX-51}) > r(\text{NaX}) > r(\text{CsNaX-60}).$$

This observation is in good agreement with the trend in the strength of the Lewis acidity of the different zeolites. On the basis of the results of these preliminary investigations, the *in situ* ^{13}C FT PFG NMR measurements have been carried out at 463 K in the case of LiNaX-51 and at 473 K in the case of NaX, CsNaX-60, and CsNaX-60 · 8CsOH.

PFG NMR Diffusion Measurements during Catalytic Reactions

Figure 5 shows the *in situ* ^{13}C FT PFG NMR spectra for the conversion of isopropanol in CsNaX-60 at a reaction time of 164 h. At this time, the propene conversion was about 38%. At the beginning of this measurement, i.e. at $g = 0$ T m^{-1}, two signals appeared: one signal at 63.1 ppm corresponding to isopropanol-2-$^{13}C_1$ and another signal at 139.9 ppm due to [$^{13}C_1$]2-propene (48). With increasing pulsed field gradient strength a decrease in the intensity of both signals due to diffusion is visible. The signal at

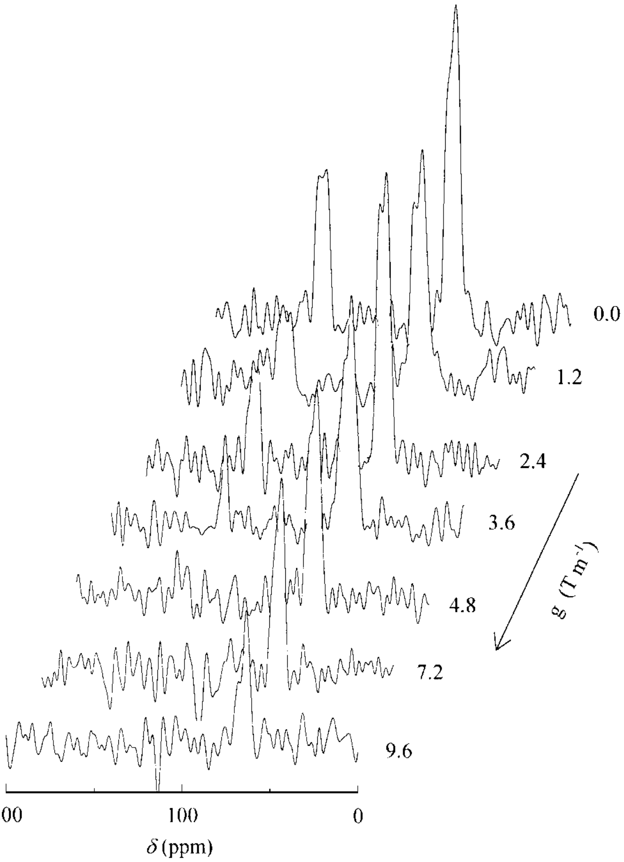

FIG. 5. *In situ* ^{13}C FT PFG NMR spectra during the reaction of $[^{13}C_1]$2-isopropanol in CsNaX-60 at 473 K as a function of the pulsed field gradient amplitude g (time of reaction, 164 h).

139.9 ppm vanished faster than the signal at 63.1 ppm corresponding to the faster diffusion of propene relative to isopropanol (45).

Figures 6 and 7 show the time dependence of the concentration of isopropanol and propene and their intracrystalline diffusivities in NaX and CsNaX-60. In both zeolites the diffusivity of isopropanol remained constant during the whole process of conversion. Simultaneously, the diffusivity of propene increased with the reaction time. This may be explained by the decrease in the hindrance by the less-mobile isopropanol molecules. From the measurements a mean self-diffusion coefficient of $(2.1 \pm 0.3) \times 10^{-10}$ m^2 s^{-1} for isopropanol in CsNaX-60 and a value of $(4.8 \pm 1.8) \times 10^{-11}$ m^2 s^{-1} for isopropanol in NaX could be determined. For comparative ^{1}H- and ^{13}C-PFG NMR measurements, a second NMR sample of NaX and CsNaX-60 with the same amount of isopropanol-2-$^{13}C_1$ was prepared and studied via ^{1}H- and ^{13}C-PFG NMR at 473 K. $[^{13}C_6]$Benzene and poly-dimethyl-siloxane were used as calibrating substances for both measurements. Figure 8 shows the attenuation plots of the relative spin echo Ψ intensity as a function of the expression $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$ for both nuclei for CsNaX-60. In agreement with Eq. [1], the attenuation plots are found to be essentially independent of the probe nucleus, yielding intracrystalline self-diffusion coefficients of $(2.0 \pm 0.5) \times 10^{-10}$ m^2 s^{-1} in the case of ^{1}H-PFG NMR and $(1.9 \pm 0.1) \times 10^{-10}$ m^2 s^{-1} in the case of ^{13}C-PFG NMR. These data are in a very good agreement with the results of the *in situ* ^{13}C Fourier transform pulsed field gradient NMR method. A similar result was obtained for NaX. It is interesting to note that, in the ^{1}H-PFG NMR measurements, a first steep decay in the spin echo attenuation plots, corresponding to the water molecules generated during the conversion process, was in no case observed. This may be explained by the fact that at the reaction temperature of 473 K the water concentration in the adsorbed phase is negligibly small in comparison with the other molecules involved in the reaction.

Via the relation

$$\tau_{\mathrm{diff.;\,intra}} = \frac{R^2}{15 \cdot D_{\mathrm{intra}}}, \qquad [2]$$

with R^2 denoting the mean square crystallite radius, the measured diffusivities might be used to determine the mean

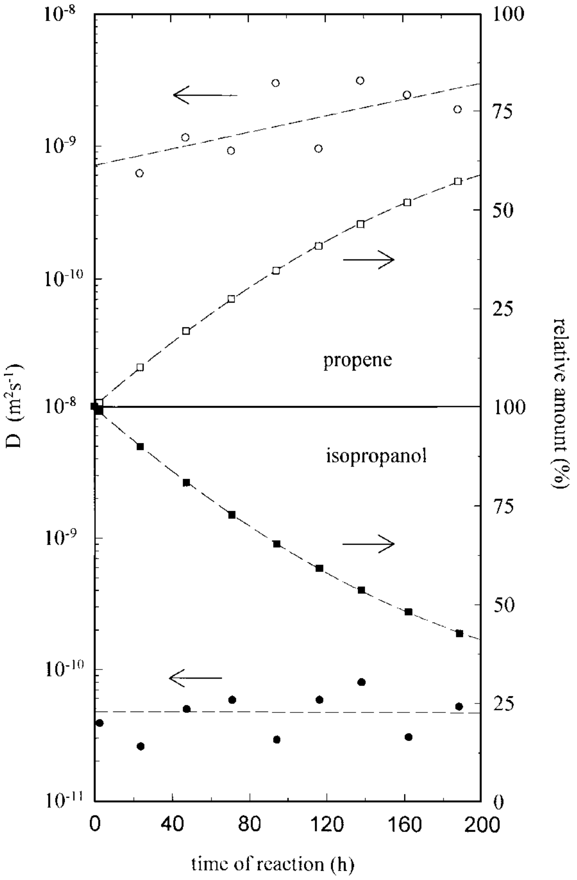

FIG. 6. Time dependence of the relative amount of isopropanol and propene during the conversion of isopropanol in NaX and their self-diffusivities at 473 K (open symbols, propene; closed symbols, isopropanol).

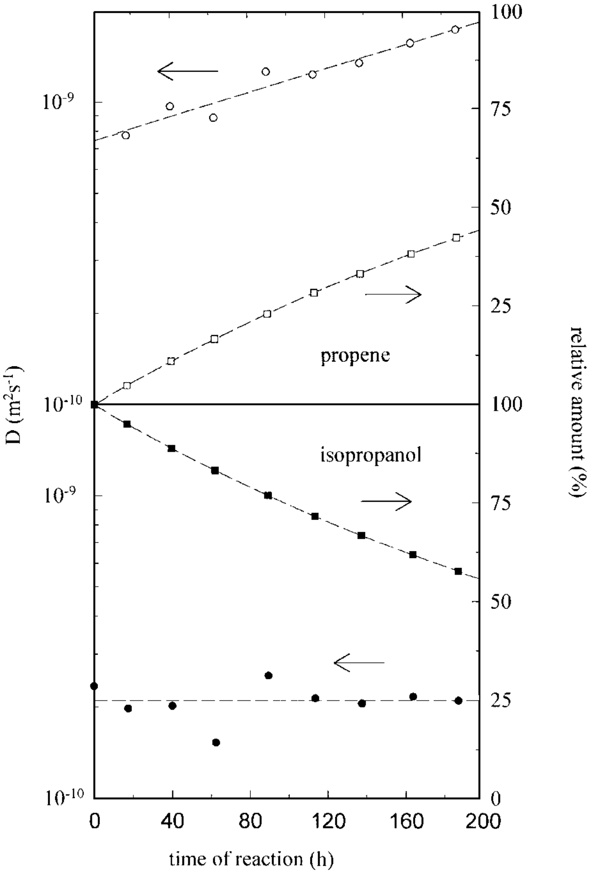

FIG. 7. Time dependence of the relative amount of isopropanol and propene during the conversion of isopropanol in CsNaX-60 and their self-diffusivities at 473 K (open symbols, propene; closed symbols, isopropanol).

lifetime $\tau_{\text{diff., intra}}$ of the reactant and product molecules within the individual crystallites assuming that the molecular exchange is exclusively controlled by intracrystalline diffusion (29). These values can be compared with the mean intrinsic reaction time τ_{reaction}. For a reaction order of one, the mean intrinsic reaction time is related to the intrinsic rate constant $k_{\text{intrinsic}}$ by

$$\tau_{\text{intrinsic}} = \frac{1}{k_{\text{intrinsic}}}. \quad [3]$$

For isopropanol, the mean lifetime and the mean intrinsic reaction time were calculated for reaction temperatures of 463 and 473 K. These values are listed in Table 2. The mean lifetime of isopropanol was about seven orders of magnitude lower than its reaction time. Any limitation of the overall reaction by intracrystalline diffusion could therefore be excluded.

Attempts were made to perform *in situ* diffusion measurements also for the conversion of isopropanol in CsNaX-60 · 8CsOH at 473 K. Unfortunately, however, the intensity of the NMR signals decreased very rapidly in the beginning of the measurements. Furthermore, an unexpected line broadening occured after a very short time of reaction. Therefore, the measurements were stopped in the hope that further investigations will clarify these problems. Nevertheless, we present here some preliminary observations from the *in situ* ^{13}C FT PFG NMR study in the zeolite CsNaX-60 · 8CsOH. During the measurement this sample became pale yellow, and the intensity of this color increased with the reaction time. In a previous publication, a similar effect was described for the same zeolite loaded with [$^{13}C_3$]1,2,3-acetone (45). In this earlier publication no direct evidence could be obtained to show that isopropanol is converted to acetone in CsNaX-60 · 8CsOH; however, the formation of acetone from isopropanol could not be conclusively excluded, because acetone, once formed, could undergo rapid consecutive reactions (37, 49, 50). Xu *et al.* (37) suggested a consecutive reaction of acetone in a CsX

TABLE 2

Intrinsic Reaction-Rate Constants ($k_{\text{intrinsic}}$), Intracrystalline Diffusion Coefficient (D_{intra}), Intracrystalline Mean Lifetime ($\tau_{\text{diff., intra}}$), and Reaction Time ($\tau_{\text{reaction}}$) of Isopropanol in Various X-Type Zeolites at 463 and 473 K

Zeolite	Crystallite size (μm)	T (K)	$k_{\text{intrinsic}}$ (s^{-1})	D_{intra} (m^2 s^{-1})	$\tau_{\text{diff., intra}}$ (s)	τ_{reaction} (s)
LiNaX-51	10	463	1.0×10^{-5}	4.1×10^{-11}	4.0×10^{-2}	1.0×10^{5}
NaX	10	473	1.3×10^{-6}	4.3×10^{-11}	3.9×10^{-2}	7.7×10^{5}
CsNaX-60	10	473	8.1×10^{-7}	5.4×10^{-11}	3.1×10^{-2}	1.2×10^{6}
CsNaX-60 · 8CsOH	10	473	7.1×10^{-6}	2.9×10^{-11}	5.7×10^{-2}	1.4×10^{5}

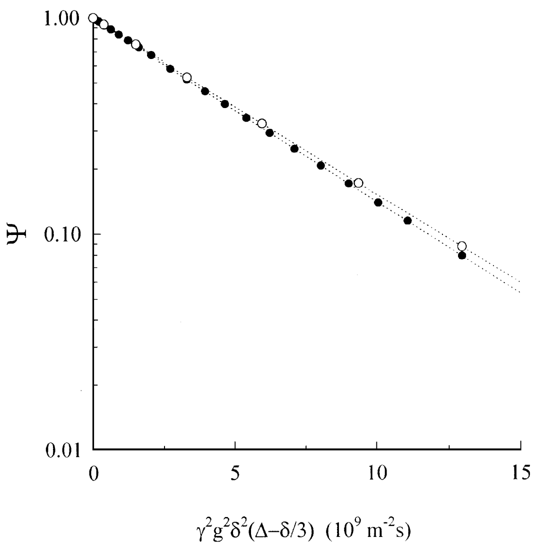

FIG. 8. Semilogarithmic plot of the relative spin echo amplitude Ψ against $\gamma^2 g^2 \delta^2(\Delta - \delta/3)$ for [$^{13}C_1$]2-isopropanol in CsNaX-60 at 473 K (open symbols, ^{13}C-PFG NMR; closed symbols, ^{1}H-PFG NMR).

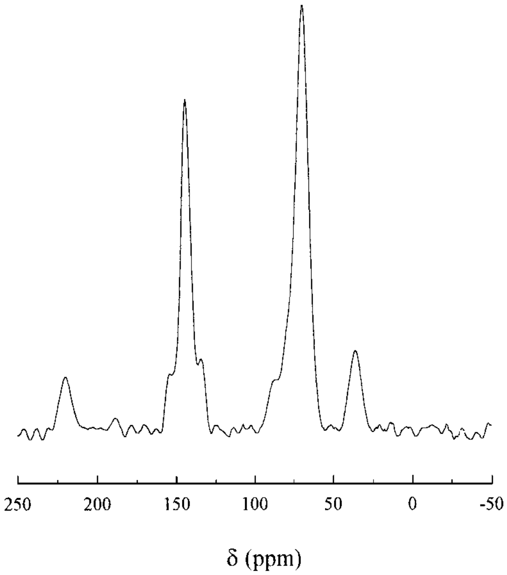

FIG. 9. ^{13}C FT NMR spectrum of $[^{13}C_1]2$-isopropanol in CsNaX-60 · 8CsOH at 541 K and at a reaction time of 40 min.

zeolite, in which acetone is converted into diacetone alcohol, mesityl oxide, phorone, isophorone, and various isomeric aromatics. Phoron is a yellow crystalline substance (51), which might give rise to the observed coloration of CsNaX-60 · 8CsOH. Röser *et al.* (52) reported an increasing selectivity of acetone in CsNaY-68 at 673 K with increasing amount of additional cesium acetate present. Obviously, an impregnation of zeolites with alkali metal oxide in the form of alkali metal acetate or alkali metal hydroxide enhances the zeolite basicity.

Figure 9 presents one ^{13}C-NMR spectrum in a series of many ^{13}C-NMR spectra which were measured to study the reaction kinetics of isopropanol in CsNaX-60 · 8CsOH at 541 K. Four signals located at $\delta_1 = 35$ ppm ($-C{=}C{-}CH_2$-region, ^{13}C-enriched at the methylene group), $\delta_2 = 63$ ppm ($-CHOH-$, $[^{13}C_1]2$-isopropanol), $\delta_3 = 140$ ppm ($-HC{=}CH-$), and $\delta_4 = 220$ ppm (carbonyl group) could be identified.

CONCLUSIONS

For the first time the diffusion of reactant and product molecules in zeolites during a catalytic reaction was investigated directly via *in situ* ^{13}C Fourier transform pulsed field gradient NMR spectroscopy. As a model reaction the conversion of isopropanol to propene (acid catalysis) or to acetone (base catalysis) was chosen. The catalysts under study were large-crystal zeolites of the faujasite type, namely LiNaX-51, NaX, CsNaX-60, and CsNaX-60 · 8CsOH. The main results of this contribution can be summarized as follows:

1. It could be shown that *in situ* ^{13}C Fourier transform pulsed field gradient NMR spectroscopy is an ideal technique for studying the diffusivity of molecules during a catalytic reaction.

2. LiNaX-51 was characterized by investigation of the diffusive behavior of selected molecules. The diffusion measurements with isopropanol, acetone, and propene led to nearly the same diffusivities for acetone and isopropanol, while the self-diffusivity of propene was significantly larger than that of the other two molecules.

3. Preliminary ^{13}C-NMR studies of the reaction behavior of isopropanol led to the following results:

—LiNaX-51, NaX, and CsNaX-60 behave like acid catalysts leading to a conversion of isopropanol to propene. CsNaX-60 · 8CsOH seemed to be a base catalyst.

—At 473 K the sequence of the reaction rate r of the three acid catalysts is arranged as

$$r(\text{LiNaX-51}) > r(\text{NaX}) > r(\text{CsNaX-60}).$$

This observation may be correlated with the strength of the Lewis acidity of these zeolites.

—The catalytic conversion of isopropanol in all zeolites under study followed a first-order reaction.

4. In contrast to propene, the self-diffusivity of isopropanol in NaX and CsNaX-60 did not depend on the reaction time. The increase of the self-diffusivity of propene with increasing conversion of isopropanol to propene could be explained in terms of the greater diffusivity of propene in comparison with that of isopropanol.

5. In NaX and CsNaX-60 any limitation of the overall reaction by intracrystalline diffusion can be excluded.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Bundesministerium für Bildung, Forschung, Wissenschaft und Technologie, under Grant 03 D 0003, as well as from Deutsche Forschungsgemeinschaft (SFB 294), Fonds der Chemischen Industrie, and Max-Buchner-Forschungsstiftung. We are particularly obliged to Dr. A. Germanus, Bruker-Franzen Analytik, Bremen, for his support in the software development for the Fourier transform PFG NMR measurements. RQS thanks the Alexander von Humboldt-Stiftung for a Research Fellowship. Helpful discussions with Professor H. Knözinger, University of Munich, are acknowledged.

REFERENCES

1. Jacobs, P. A., and Martens, J. A., *Stud. Surf. Sci. Catal.* **58**, 445 (1991).
2. Venuto, P. B., *Microporous Mat.* **2**, 297 (1994).
3. Dartt, C. B., and Davis, M. E., *Ind. Eng. Chem. Res.* **33**, 2887 (1994).
4. Sidorenko, Y. N., Galich, P. N., Gutyrya, V. S., Il'in, V. G., and Neimark, I. E., *Dokl. Akad. Nauk SSSR* **173**, 132 (1967).
5. Yashima, T., Soto, K., Hayasaka, H. T., and Hara, N., *J. Catal.* **26**, 303 (1972).
6. Sefcik, M. D., *J. Am. Chem. Soc.* **101**, 2164 (1979).
7. Itoh, H., Miyamoto, A., and Murakami, Y., *J. Catal.* **64**, 284 (1980).
8. Engelhardt, J., Szanyi, J., and Valyon, J., *J. Catal.* **107**, 296 (1987).
9. Hathaway, P. E., and Davis, M. E., *J. Catal.* **119**, 497 (1989).
10. Slaugh, L. H., and Brownscombe, T. F., U.S. Patent 5 015 796, 1991.

11. Philippou, A., and Anderson, M. W., *J. Am. Chem. Soc.* **116**, 263 (1989).
12. Yashima, T., Suzuki, H., and Hara, N., *J. Catal.* **33**, 486 (1974).
13. Hathaway, P. A., and Davis, M. E., *J. Catal.* **138**, 164 (1992).
14. Dessau, R. M., *Zeolites* **10**, 205 (1990).
15. Coughlan, B., and Keane, M. A., *J. Catal.* **138**, 164 (1992).
16. Huang, M., Zielinski, P. A., Moulod, J., and Kaliaguine, *Appl. Catal. A* **118**, 33 (1994).
17. Rode, E. J., Gee, P. E., Marquez, L. N., Uemura, T., and Bazargani, M., *Catal. Lett.* **9**, 103 (1991).
18. Kim, J. C., Li, H.-X., Chem, C.-Y., and Davis, M. E., *Microporous Mat.* **2**, 413 (1994).
19. Gortsema, F. P., Sharkey, J. J., Wildman, G. T., and Beshty, B. S., European Patent Application 481 674 A1, 1992.
20. Gortsema, F. P., Beshty, B. S., Friedman, J. J., Matsumoto, D., Sharkey, J. J., Wildman, G., Blacklock, T. J., and Pan, S. H., *in* "Catalysis of Organic Reactions" (J. R. Kosak and T. A. Johnson, Eds.), p. 445. Dekker, New York, 1994.
21. Brownscombe, T. F., U.S. Patent 4 992 613, 1991.
22. Huang, M., and Kaliaguine, S., *Catal. Lett.* **18**, 373 (1993).
23. Berkani, M., Lemberton, J. L., Marczewski, M., and Perot, G., *Catal. Lett.* **33**, 405 (1995).
24. Burger, B., Dissertation, University of Stuttgart, 1995.
25. Romannikov, V. N., *J. Mol. Catal.* **98**, 57 (1995).
26. Okamoto, Y., Ogawa, M., Maezawa, A., and Imanaka, T., *J. Catal.* **112**, 427 (1988).
27. Vinek, H., Noller, H., Ebel, M., and Schwarz, K., *J. Chem. Soc. Faraday Trans.* **73**, 734 (1977).
28. Grünert, W., Muhler, M., Schröder, K.-P., Sauer, J., and Schlögl, R., *J. Phys. Chem.* **98**, 10920 (1994).
29. Kärger, J., and Ruthven, D. M., "Diffusion in Zeolites and Other Microporous Solids." Wiley, New York, 1992.
30. Chen, N. Y., Degnan, T. F., and Smith, C. M., "Molecular Transport and Reaction in Zeolites." VCH, New York, 1994.
31. Hong, U., Kärger, J., Hunger, B., Feoktistova, N. N., and Zhdanov, S. P., *J. Catal.* **137**, 243 (1992).
32. Haw, J. F., Richardson, B. R., Oshiro, I. S., Lazo, N. D., and Speed, J. A., *J. Am. Chem. Soc.* **111**, 2052 (1989).
33. Richardson, B. R., Lazo, N. D., Schettler, P. D., White, J. L., and Haw, J. F., *J. Am. Chem. Soc.* **112**, 2886 (1990).
34. Lazo, N. D., Richardson, B. R., Schettler, P. D., White, J. L., and Haw, J. F., *J. Phys. Chem.* **95**, 9420 (1991).
35. Munson, E. J., Kheir, A. A., Lazo, N. D., and Haw, J. F., *J. Phys. Chem.* **96**, 7740 (1992).
36. Murray, D. K., Chang, J.-W., and Haw, J. F., *J. Phys. Chem.* **115**, 4732 (1993).
37. Xu, T., Munson, E. J., and Haw, J. F., *J. Phys. Chem.* **116**, 1962 (1994).
38. Anderson, M. W., and Klinowski, J., *J. Am. Chem. Soc.* **112**, 10 (1990).
39. Hunger, M., and Horvath, T., *J. Chem. Soc. Chem. Comm.* 1423 (1995).
40. Ernst, H., Freude, D., Mildner, T., and Wolf, I., *Solid State NMR* **6**, 147 (1996).
41. Snurr, R. Q., Hagen, A., Ernst, H., Schwarz, H. B., Ernst, S., Weitkamp, J., and Kärger, J., *J. Catal.*, in press.
42. Charnell, J. F., *J. Cryst. Growth* **8**, 291 (1971).
43. Kärger, J., Bär, N.-K., Heink, W., Pfeifer, H., and Seiffert, G., *Z. Naturforsch.* **50a**, 186 (1995).
44. Kärger, J., Pfeifer, H., and Heink, W., *Adv. Magn. Reson.* **12**, 1 (1988).
45. Schwarz, H. B., Ernst, H., Ernst, S., Kärger, J., Röser, T., Snurr, R. Q., and Weitkamp, J., *Appl. Catal. A* **130**, 227 (1995).
46. Fick, A. E., *Ann. Phys.* **94**, 59 (1855).
47. Fick, A. E., *Phil. Mag.* **10**, 30 (1855).
48. Hesse, M., Meier, H., and Zech, B., "Spektroskopische Methoden in der organischen Chemie," p. 171. Thieme, Stuttgart, 1987.
49. Martens, L. R., Vermeiren, W. J., Huybrechts, D. R., Grobet, P. J., and Jacobs, P. A., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternam, Eds.), Vol. 1, p. 420. Chem. Institute of Canada, Ottawa, 1988.
50. Hoelderich, W. F., and van Bekkum, H., *Stud. Surf. Sci. Catal.* **58**, 631 (1991).
51. D'Ans-Lax, "Taschenbuch für Chemiker und Physiker," Bd. II, p. 671. Springer, Berlin, 1983.
52. Röser, T., Ernst, S., and Weitkamp, J., *in* "7th German Zeolite Conference." Konstanz, Germany, March 20–22, 1995.