

# RELAXATION- AND SELF-DIFFUSION MEASUREMENTS OF SOME HYDROCARBONS AND WATER AND METHANOL ON SILICALITE AND ZSM 5 ZEOLITES

H. LECHERT , J. Wienecke , W.D. Basler

Institute of Physical Chemistry, University of Hamburg  
Laufgraben 24, 2000 Hamburg 13, Germany

## ABSTRACT

The mobility mechanisms of water, methanol, butene, and a series of n-hydrocarbons from butane to dodecane have been studied in silicalite and two samples of ZSM 5 with Si/Al = 18 and 169 by the proton relaxation times  $T_1$  and  $T_2$  and self diffusion measurements. The self diffusion coefficient could be measured only for water and butene in silicalite. Both values are  $3 \cdot 10^{-4}$  cm<sup>2</sup>/s at 400 K. The activation energies are 31 resp. 12 kJ/mole.

Water and methanol in silicalite show an almost isotropic reorientation. In ZSM 5 the motion becomes anisotropic, especially in the Na-forms, and the  $T_1$ -minima are shifted to higher temperatures. The motion of the hydrocarbons is severely restricted in all samples and strongly anisotropic with rotational reorientation. Butene is bound very tightly with restrictions even of the rotational motions both in Na- and in H-ZSM 5.

## INTRODUCTION

The great importance of the ZSM 5 type zeolites for the application lies in the peculiarities of the pore structure causing special selectivity effects in catalysis. The different mechanisms of interaction of the adsorbed molecules with the walls of the channels of the aluminosilicate structure and with the cations and the OH-groups have been studied previously by careful sorption experiments /1/.

The present paper shall be devoted to investigations of the mobility of water, methanol, 1-butene and the n-hydrocarbons from butane to dodecane by pulsed NMR-methods. These substances represent the most important types of compounds involved in the wellknown methanol reaction catalyzed preferably by ZSM 5 type zeolites.

As adsorbends two samples of ZSM 5 with Si/Al = 18 and 169 and a silicalite sample are used. In the silicalite sample only the inter-

actions with the silica surface inside the channels is measured and may be compared with the influences originating from the Na-ions and the OH groups in the H-forms of the ZSM 5 samples.

The molecular motion is studied by the H-NMR-relaxation times  $T_1$  and  $T_2$  to obtain the correlation time of the molecular reorientation. This correlation time is the period in which fixed spatial relations of the H-nuclei are given. Therefore, the temperature dependence of  $T_1$  and  $T_2$  gives information about the activation energies and the kind of the molecular motion. In favourable cases the translational motion e.g. the self diffusion can be studied by the pulsed field gradient technique /2/.

The mentioned selectivity phenomena are closely related to the restrictions of the motional freedom of the educts and products in the catalytic process. Therefore, information about molecular motion obtained from NMR-data should give valuable insight into the influences of the pore structure of ZSM 5 zeolites on the kinetics of the catalytic reaction.

#### EXPERIMENTAL

Samples used. The samples used in the NMR-experiments have been synthesized in our laboratory. In order to obtain large ZSM 5 crystals a batch composition has been used containing  $\text{Li}_2\text{O}$  as described by Nastro and Sand /3/. The batch compositions of the different samples are given in Table 1.

Table 1

Batch compositions of the synthesis of the zeolite samples

Sample	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$	TPA/ $\text{SiO}_2$	$\text{NH}_4\text{OH}/\text{SiO}_2$	$\text{H}_2\text{O}/\text{SiO}_2$	t °C
Z18	59	1	0.14	1.28	12.7	180
Z169	168	1	0.14	1.28	12.7	180
S	$\infty$	0	0.06	NaOH/ $\text{SiO}_2$ 0.03	10.5	95

TPA means the tetrapropylammonium ion.

The samples are characterized by Z for ZSM 5 and by S for silicalite. The number behind the Z gives the Si/Al-ratio of the final product. The analyses of the final products were done by AAS. The Z-samples contained no Li and had Fe-contents of 220 ppm for Z169 and 70 ppm for Z18. The S-sample had 220 ppm Fe-impurity.

The crystallinity was checked by X-ray measurements. All samples showed good crystallinity. Z18 could be shown to consist of needles of an average length of 25  $\mu\text{m}$ , Z169 consists of needles of 10  $\mu\text{m}$ .

The S sample had crystals of a nearly spherical shape with a diameter of 10  $\mu\text{m}$ .

After calcination in air at 500°C the H- and Na-ZSM 5 were obtained by treating the samples with 0.1 M HCl or 0.1 M NaCl solution.

The dehydration of the samples was done at 400°C at a vacuum of 1 mPa for 12 hours. The degree of dehydration was checked gravimetrically. The sorbates water and methanol were purified from air by several freeze-pump-thaw cycles. The gases butane and butene were taken from Merck "minicans" without any purification. The sorption was performed via the gas phase. The amount of sorbed substance was checked gravimetrically and is given in the legends of the figures.

The NMR experiments were carried out with a BRUKER BKR 322 spectrometer at 60 MHz.  $T_1$  was obtained using the 180°-90°-pulse sequence.  $T_2$  less 1 ms were taken from the free induction decay, longer  $T_2$  from the Carr-Purcell-sequence.

The self diffusion coefficients have been measured by the pulsed field gradient technique /4/.

## RESULTS

In Fig.1 the temperature dependence of  $T_1$  and  $T_2$  of water, methanol, butane, and butene in silicalite is given. All four substances show motional narrowing of  $T_2$ , and  $T_1$ -minima. For water a broad  $T_1$ -minimum near 200 K is observed. The  $T_1$ -minimum of methanol is near 230 K and more pronounced.  $T_1$ -minima of butane and butene are found near 260 K. The absolute values of  $T_1$  of several milliseconds indicate interaction with paramagnetic Fe-impurities. Low temperature  $T_2$  at 160 K of water, methanol, and butene are about 30  $\mu\text{s}$  which is three times longer than the expected rigid lattice value of nearly 10  $\mu\text{s}$ . In contrast,  $T_2$  of butane is 100  $\mu\text{s}$  at 160 K. This indicates at least narrowing of the intramolecular H-H-interaction by rotational motion even at 160 K, especially in case of butane.

Because at least in case of  $T_2$  the contribution of the H-H- and the H-Fe-interaction may vary with temperature no reliable activation energies can be obtained from the slope of  $\log T_2$  vs. inverse temperature.

In Fig.2 the results for butene in Na-Z169 and butane in Na- and H-Z169 are shown. The values of butene in Na- and H-Z18 are nearly identical with those in H-Z169, the values of butane in Na- and H-Z18 and in H-Z169 with those in Na-Z169, and therefore not shown.

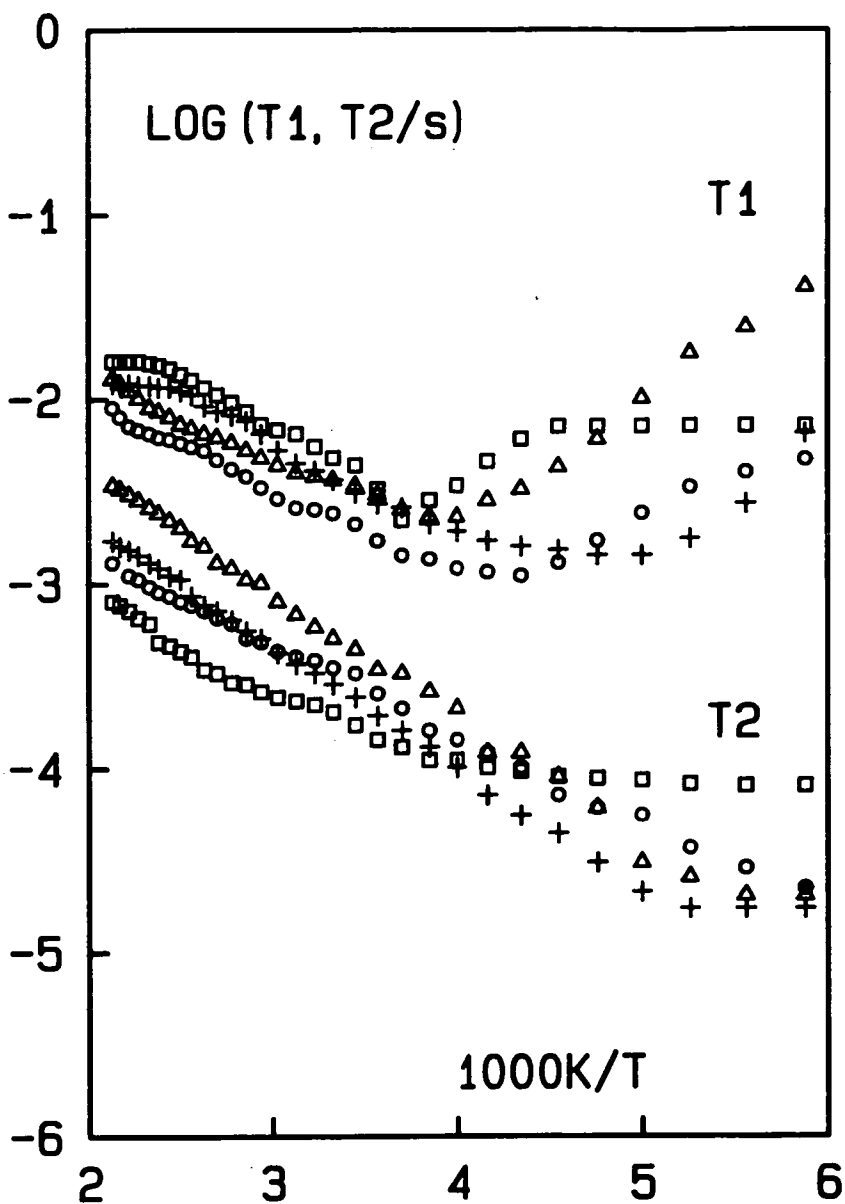


Fig. 1. Temperature dependence of the longitudinal ( $T_1$ ) and transverse ( $T_2$ ) proton relaxation times of  $\blacktriangle$  4.0 mmol water,  $\bullet$  3.5 mmol methanol,  $\blacksquare$  1.3 mmol butane, and  $\blacktriangleleft$  1.9 mmol butene per g silicalite.

$T_2$  of butene increases to about 1 ms only in Na-Z169 but remains constant at 30  $\mu$ s in all other samples. The  $T_1$ -minimum of butene is near 290 K in Na-Z169 and shifted to 330 K in H-Z169. In all samples the  $T_1$  minima of butane are near 290 K and all  $T_2$ 's increase from 0.1 ms at 160 K to 0.5 ms at 470 K.

In Fig.3 water and methanol Na-Z18 and Na-Z169 are compared. Similar results were found for H-Z18 resp. H-Z169 and are not shown. Whereas all  $T_2$ 's are increasing with temperature only  $T_2$  of water in Na-Z169 is constant at 0.2 ms between 160 and 350 K and then increasing. All  $T_1$ -minima are broad and in the range of 250 to 300 K.

The coefficient of self diffusion of water and butene in silicalite, determined the NMR pulsed field gradient technique is given in Table 2.

Table 2

Self diffusion of water and butene in silicalite

T/K	360	380	400	420	
$D/10^{-8} \text{ m}^2/\text{s}$	1.2	1.7	3.0	4.8	water
	2.2	2.8	3.2	4.0	butene

The corresponding activation energy of diffusion is  $31 \pm 2$  kJ/mole for water and  $12 \pm 2$  kJ/mole for butene.

## DISCUSSION

The wellknown hydrophobic character of silicalite /5/ can be clearly seen by the relaxation times (Fig.1) and the self diffusion (Table 2). The  $T_1$ -minima, where the correlation time of molecular reorientation is about  $10^{-9}$  s, are increasing in the order water-methanol-butene-butane from 200 to 260 K. For comparison the  $T_1$ -minimum of water in Na-faujasite is near 260 K. The self diffusion of water can be extrapolated to  $2 \cdot 10^{-9} \text{ m}^2/\text{s}$  at 300 K which is nearly the value of the pure liquid and ten times faster than in Na-X faujasite /6/.

Butene ( $D = 10^{-9} \text{ m}^2/\text{s}$  at 300 K) is hundred times more mobile in silicalite than in Na-X /7/. No significant difference between the temperatures of  $T_1$ -minima of butane and butene could be observed (Fig.1). Both observations can be explained by the fact that there are no cations in silicalite for specific interaction with the  $\pi$ -bond of butene.

Methanol which has both hydrophobic and hydrophilic parts in its molecule show a behaviour intermediate between water and the hydrocarbons.

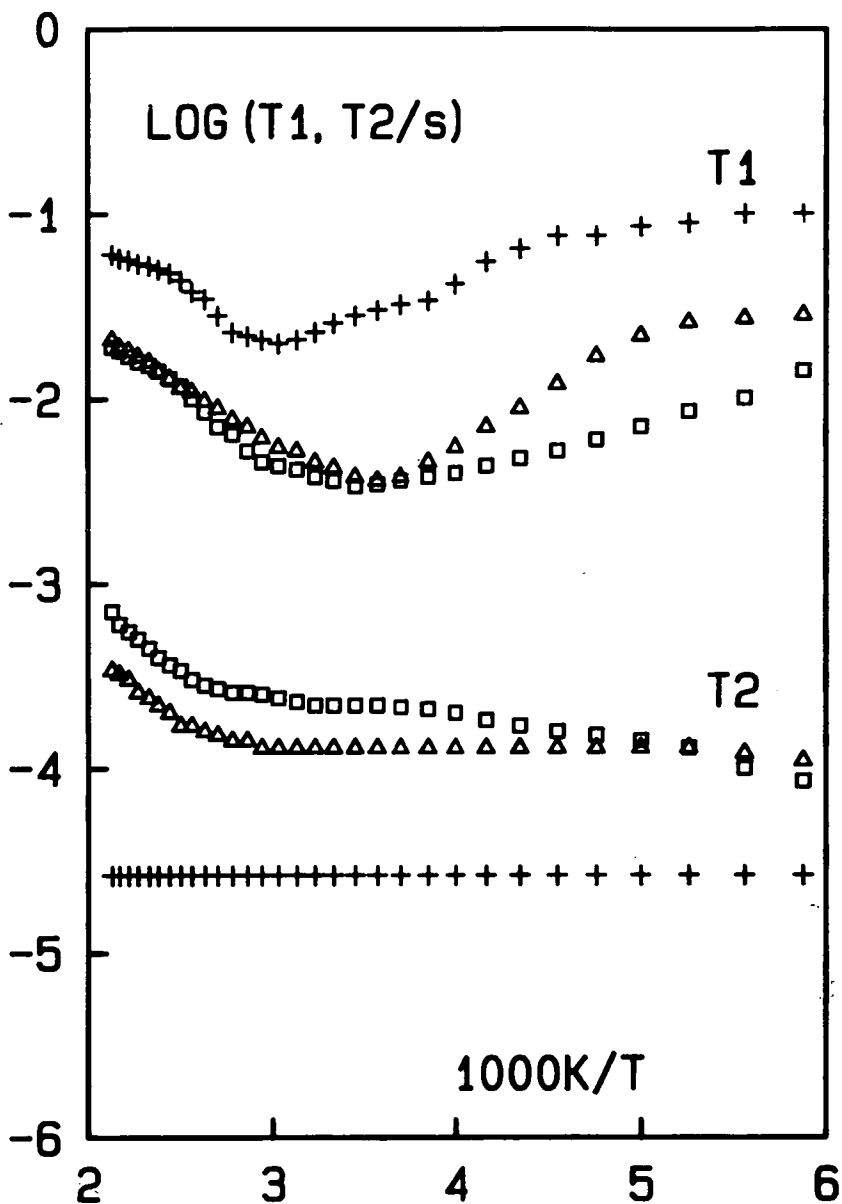


Fig. 2. Temperature dependence of the longitudinal ( $T_1$ ) and transverse ( $T_2$ ) proton relaxation times of butane and butene in ZSM 5 with Si/Al = 169 (Z169):

▲ 1,0 mmol butane/g Na-Z169, + 1.0 mmol butene/g H-Z169, and ■ 1.4 mmol butene/g Na-Z169.

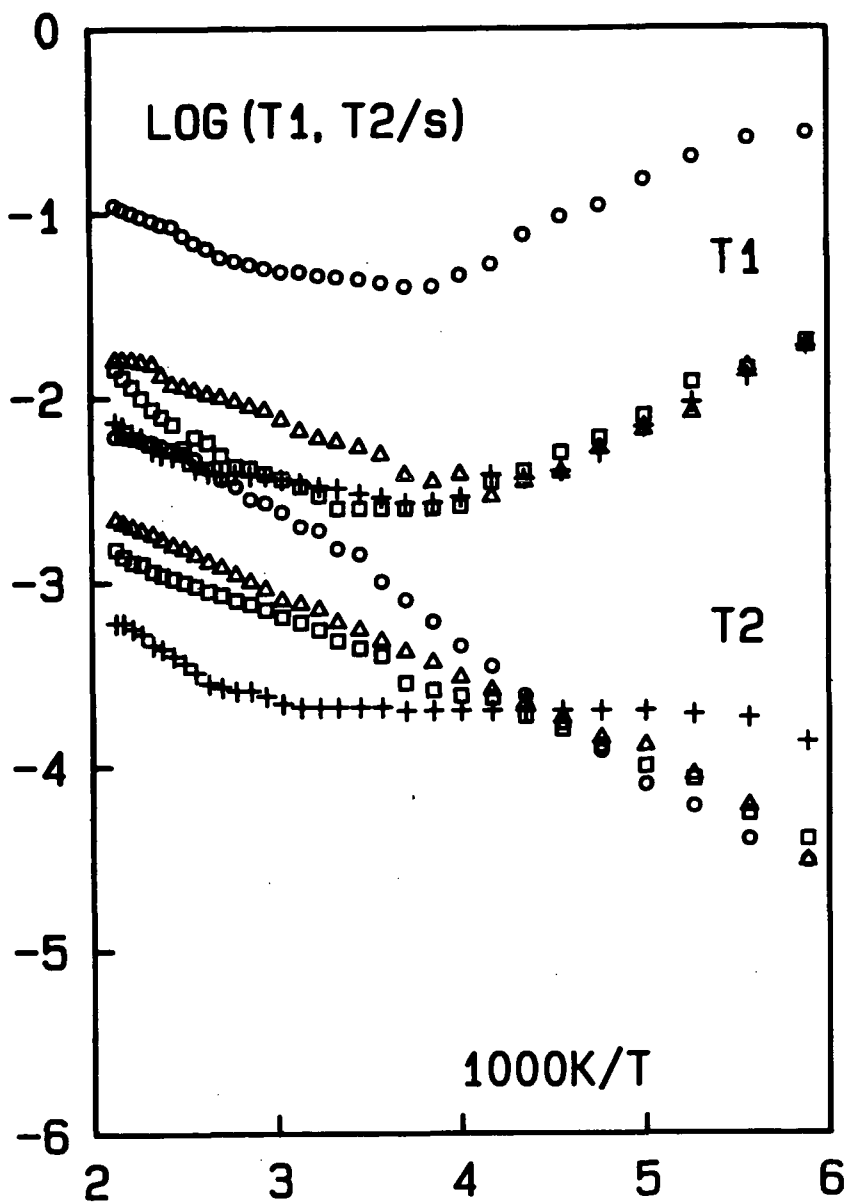


Fig. 3. Temperature dependence of the longitudinal ( $T_1$ ) and transverse ( $T_2$ ) proton relaxation times of water and methanol in Na-ZSM 5 with Si/Al = 18 (Z18) and Si/Al = 169 (Z169):  $\blacktriangle$  3.0 mmol water/g Na-Z18,  $+$  4.0 mmol water/g Na-Z169,  $\circ$  4.3 mmol methanol/g Na-Z18, and  $\blacksquare$  3.8 mmol methanol/g Na-Z169.

The low temperature values of  $T_2$  of all four substances are well above the expected rigid lattice value of 10  $\mu\text{s}$ . Therefore their correlation time of the molecular reorientation must be shorter than  $10^{-5}$  s at 160 K.

The possible influence of the cations on the sorbate-sorbend-interaction should become apparent comparing silicalite, Z169 and Z18 differing largely in the concentration of Na-ions resp. H-ions. In case of butane no significant difference has been observed for all sorbends, indicating that only non-specific hydrophobic interaction occurs with the zeolite framework.

For butene  $T_2 = 30 \mu\text{s}$  is observed up to 470 K, hence there is strong restriction of molecular reorientation in H-Z18, Na-Z18 and also in H-Z169. In Na-Z169 almost no difference between butane and butene can be found (Fig.2). This shows strong interaction between butene and the H-ions. Even the ratio of 1 H-ion to 10 molecules butene in H-Z169 is sufficient to prevent isotropic reorientation.

For Na-Z18 with 1 Na-ions per butene a similar restriction of molecular reorientation takes place but obviously not in Na-Z169. In agreement with these findings the same molecular correlation time of butene in H-Z18, H-Z169 and Na-Z18 is reached at a higher temperature ( $T_{1\text{min}}$  at 330 K) than in Na-Z169 ( $T_{1\text{min}}$  at 290 K). Nevertheless, even at the corresponding temperatures of  $T_{1\text{min}}$  the reorientation is much more anisotropic in the samples with  $T_2 = 30 \mu\text{s}$ .

In addition the  $T_1$  and  $T_2$  relaxation times of n-paraffins with  $C = 6, 8, 10, \text{ and } 12$  were measured between 120 and 470 K. Low temperature  $T_2$  were about 20  $\mu\text{s}$ . Depending on the chain length,  $T_2$  started increasing at temperatures between 180 and 350 K to a final value of 250  $\mu\text{s}$ . The  $T_1$ -minima were broad and situated near 290 K, no systematic variation with C-number could be observed. It can be concluded that the reorientation of n-paraffins with C-number above 6 is severely restricted by the linear channel structure of ZSM 5 whereas butane and probably the shorter n-paraffins may reorient isotropically in the channel intersections.

Finally, the influence of Na-ions on water and methanol was studied by comparing Na-Z18 with Na-Z169 (Fig.3) and silicalite (Fig.1). Going from silicalite to ZSM 5 the  $T_1$ -minimum is shifted from 200 to 260 K but no significant difference is observed between Na-Z18 and Na-Z169. Nevertheless,  $T_2$  indicates more isotropic reorientation at low temperatures in Na-Z169 with less Na-ions whereas at higher temperatures a shorter  $T_2$  is caused by the higher Fe-content of Na-Z169.



Like in the case of water the  $T_1$ -minimum of methanol is shifted from 230 K in silicalite to about 270 - 290 K in ZSM 5 but no marked difference between Na-Z18 and Na-Z169 can be seen. Evidently already a concentration of 1 Na-ion per 40 molecules of water resp. methanol is sufficient to create the remarkable difference between ion-free silicalite and Na-ZSM 5. Further increase of Na-content seems to be less effective.

The ratio of the  $T_1$  values of Na-Z169 and Na-Z18 is about 10 whereas the ratio of the analytical Fe-contents is 3. This allows the conclusion that not all Fe in ZSM 5 is equally effective in NMR relaxation and hence should be located in sites with different accessibility.

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