

## COMMUNICATIONS TO THE EDITOR

### Kinetics of Ammonia Penetrating into the Sodalite Units of Sodium Faujasites Studied by Nuclear Magnetic Resonance

*Sir:* Faujasites and type A zeolites contain two different kinds of intracrystalline voids, i.e., a system of large pores interconnected in three dimensions and small pores in the interior of the sodalite building units of the aluminosilicate framework. As access from large pores into small pores is possible only through six-membered rings of 0.25-nm free aperture, only small molecules such as water or ammonia can penetrate into the sodalite units.

It has been found that water molecules in small pores can be detected and measured separately from those in large cavities by pulsed proton NMR, as they give rise to a fast decaying part ( $T_2 \approx 25 \mu\text{s}$ ) in the free induction decay.<sup>1-3</sup> By this method the kinetics of water molecules entering<sup>4,5</sup> and leaving<sup>6</sup> the sodalite units of faujasites has been determined as a function of temperature and activity. Some first experiments with ammonia showed essentially the same effects as in case of water.<sup>4</sup> Consequently corresponding NMR studies have been performed with ammonia, too.

The zeolites used were Na-X (Linde 13X of Union Carbide Corp., Si/Al = 1.18) and Na-Y (self-made, Si/Al = 2.36). After outgassing (pressure less 1 mPa for 24 h at 670 K) the samples were loaded with purified ammonia from a zeolitic reservoir at 273 K. After loading no fast decaying part has been observed in the free induction decay at a detection limit of 1%. Then different parts of the same sample were stored at temperatures between 370 and 470 K and the intensity of the fast decaying part of the NMR signal has been measured as a function of storing time.

In Figure 1 two typical NMR signals (magnetization vs. time) are shown for Na-Y, signals for ammonia in Na-X can be found in ref 4.

As in case of water, the small, fast decaying part of the NMR signal is attributed to intact ammonia molecules in the sodalite units. The reasons are as follows:

1. By Fourier transforming the continuous wave spectrum of rotating ammonia molecules, found by Deininger and Reimann for ammonia in the large pores of faujasites at 77 K,<sup>7</sup> an oscillating relaxation function (minimum after 35  $\mu\text{s}$ , maximum after 55  $\mu\text{s}$ , decaying to 10% after 100  $\mu\text{s}$ ) is obtained. The fast decaying part of the signal shows well the predicted shape in case of Na-Y at 295 K, as can be seen in Figure 1, upper curve. In Na-X the relaxation is slower at 295 K, but the predicted shape is found for  $T < 250 \text{ K}$ , too. This agrees with the observation that water molecules in the sodalite units of Na-X are more mobile than in those of Na-Y.<sup>9</sup>

2. The signal cannot be caused by protons by OH groups, as these protons do not have an oscillating relaxation function.

3. The concentration of OH groups or structural defects, where ammonia could be bound strongly, is at least one order of magnitude smaller in the sodium faujasites used<sup>4</sup> than the intensity of the signal (up to 1  $\text{NH}_3$  per cage).

4. Binding to OH groups or defects should take place immediately, whereas all zeolites did not show the fast

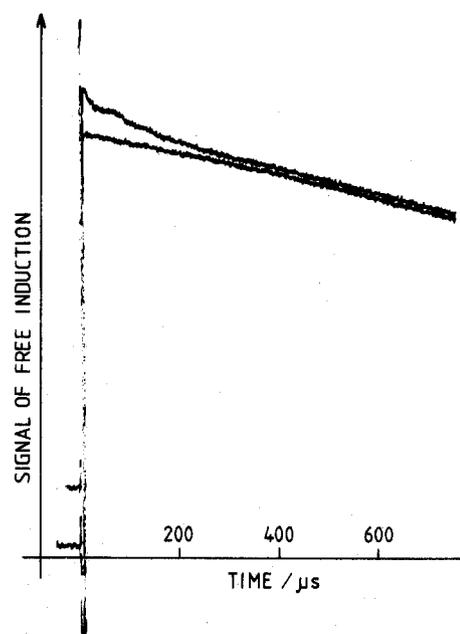


Figure 1. Proton NMR free induction decay of 77 mg of  $\text{NH}_3/\text{g}$  of Na-Y, Si/Al = 2.36,  $T = 295 \text{ K}$ , sweep = 800  $\mu\text{s}$ ; upper curve, after 32 h at 430 K; lower curve, after 6 months at 295 K.

TABLE I: Number of Ammonia Molecules Sorbed Per Sodalite Unit and Half-Time of Penetration as Studied by Proton NMR<sup>a</sup>

zeolite	Na-X		Na-Y		T/K
mg of $\text{NH}_3/\text{g}$	58	118	172	50	77
$p(\text{NH}_3)$ , Pa	15 <sup>a</sup>	300	14000		295
fast decaying part, %	9	10	6	10.5	10
molecules of $\text{NH}_3$ per sodalite unit	0.51	1.17	1.05	0.48	0.73
half-time $t_{1/2}$ , h	>300	30		>300	370
	30	2	<0.2		25
	5	<0.2			7
	<0.2	<0.2			<0.2
					470

<sup>a</sup> Estimated from ref 10.

decaying signal when freshly loaded at 273 K.

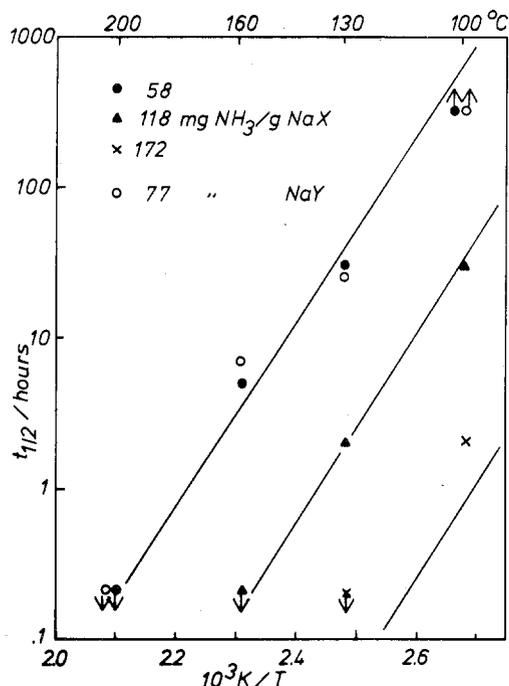
5. In faujasites with no cations in the six-membered rings, i.e., free access to the sodalite units, the signal has been observed immediately after loading.<sup>4</sup> The intensity was at most 10% of the total signal. Therefore the function of attaining sorption equilibrium could not be determined unambiguously, it seemed to be exponential. From a plot of the intensity vs. time the time  $t_{1/2}$  to obtain half of the equilibrium intensity was taken with errors up to 50%.

All experimental data can be found in Table I.

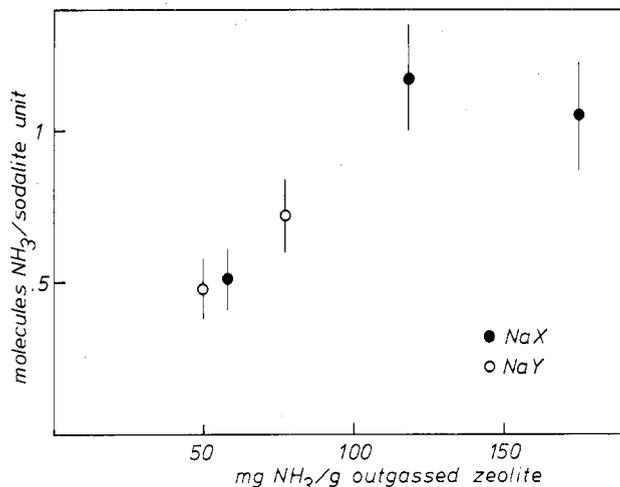
At fixed loading and activity  $a$ , an Arrhenius law for the rate and hence  $t_{1/2}$  can be assumed:

$$t_{1/2} = t_0(a) \exp(E_A/RT) \quad (1)$$

As can be seen from Figure 2, an activation energy  $E_A$  of  $120 \pm 10 \text{ kJ/mol}$  is found. This is definitely greater than the value of  $90 \pm 10 \text{ kJ/mol}$  found for water in sodium faujasites.<sup>4</sup>



**Figure 2.** Arrhenius plot of the half-time  $t_{1/2}$  of ammonia penetrating into sodalite units of sodium faujasites: (●) 58, (▲) 118, (X) 172 mg of  $\text{NH}_3/\text{g}$  of outgassed Na-X, (○) 77 mg of  $\text{NH}_3/\text{g}$  of Na-Y. Solid lines are plots of eq 1 and 2 with  $E_A = 120$  kJ/mol and  $\tau_0 = 10^{-16}$  s.



**Figure 3.** Equilibrium number of ammonia molecules per sodalite unit for different amounts of loading: (●) Na-X, (○) Na-Y.

As in faujasites with no cations in the center of the six-membered rings even ammonia passed rapidly into the sodalite units ( $t_{1/2}$  less 10 min at 300 K),<sup>4</sup> the observed activation energy should be connected with the removing of the sodium ion from the six-membered rings by interaction with the ammonia molecules sorbed in the large pores. The difference of the activation energy between water and ammonia agrees well with the difference of the energy of interaction of one of these molecules with sodium ions, calculated by Barrer and Bratt as 28 kJ/mol.<sup>8</sup>

By comparing the rate at different amounts of loading, the assumption of a first-order reaction with respect to the activity  $a = p/p_0$ , where the vapor pressure of ammonia at 295 K is taken for  $p_0$ , i.e.

$$t_0(a) = \tau_0 a^{-1} \quad (2)$$

is seen to be well fulfilled (solid lines in Figure 2) with  $a\tau_0 \approx 10^{-16}$  s.

The extrapolation of the half-times agrees with the

observation that a sample of 65 mg of  $\text{NH}_3/\text{g}$  of NaX shows no fast decaying part in the signal (<1%) after 2 years at ambient temperature, giving  $t_{1/2} > 10^5$  h (extrapolation gives  $10^7$  h).

The maximum intensity of the fast decaying part after sorption equilibrium has been reached yielded 1 ammonia molecule per sodalite unit, which is reached for loadings greater 100 mg of  $\text{NH}_3/\text{g}$  (Figure 3).

As in the case of water, we could not observe any difference of the rate between Na-X and Na-Y (see Table I and Figures 1-3). This is to be expected since all six-membered rings are occupied by sodium cations in this Si/Al ratio range.

## References and Notes

- (1) H. Pfeifer, *Surface Sci.*, **52**, 434 (1975).
- (2) J. S. Murday, R. L. Patterson, H. A. Resing, J. K. Thompson, and N. H. Turner, *J. Phys. Chem.*, **79**, 2674 (1975).
- (3) W. D. Basler, H. Lechert, and H. Kacirek, *Ber. Bunsenges. Phys. Chem.*, **80**, 451 (1976).
- (4) W. D. Basler, *ACS Symp. Ser.*, **No. 34**, 291 (1976).
- (5) W. D. Basler, *ACS Symp. Ser.*, **No. 40**, 335 (1977).
- (6) W. D. Basler, *Ber. Bunsenges. Phys. Chem.*, **82**, 1051 (1978).
- (7) D. Deininger and B. Reimann, *Z. Phys. Chem. (Leipzig)*, **251**, 53 (1972).
- (8) R. M. Barrer and C. C. Bratt, *J. Phys. Chem. Solids*, **12**, 130 (1959).
- (9) W. D. Basler, manuscript in preparation.
- (10) O. Grubner, P. Jiru, and M. Ralek, *Molekularsiebe*, VEB Deutscher Verlag der Wissenschaften, Berlin, 1968, p 96.

Institute of Physical Chemistry  
of the University of Hamburg  
2000 Hamburg 13, West Germany

Wolf D. Basler\*  
Thomas Bein

Received November 22, 1978

## Determination of the Rate Constant of the Reaction

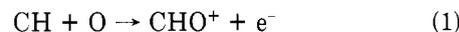
### $\text{CH} + \text{O} \rightarrow \text{CHO}^+ + \text{e}^-$ at 295 K

Publication costs assisted by the Belgian "National Fonds voor Wetenschappelijk Onderzoek"

Sir: As has been shown extensively in the literature<sup>1-3</sup> the saturation current technique yields very useful information about chemi-ionization phenomena occurring in the oxidation process of hydrocarbons. Indeed, this method provides a direct measurement of the chemi-ionization reaction rate  $U_+$  which is related to the saturation current  $i_s$  according to

$$U_+ = \frac{i_s}{Ve} \quad (1)$$

where  $V$  is the volume of the entire reaction zone and  $e$  the electronic charge. Since reaction 1 is in general



considered to be the primary chemi-ionization reaction in hydrocarbon oxidations, the rate of this reaction  $U_+$  is equal to  $k_1[\text{CH}][\text{O}]$ . While the concentrations, the corresponding saturation currents, and hence  $k_1$  have been measured in a series of low pressure methane and ethylene flames<sup>4</sup> at temperatures near 2000 K, no such data were available at room temperature. We now report the measurement of  $k_1$  in a fast flow reactor under the same experimental conditions as in which we have measured  $i_s$ .<sup>3</sup> The cylindrical Pyrex reactor has an inner diameter of 16 mm, and a reacting mixture was investigated containing 3 mtorr of acetylene, 5.5 mtorr of atomic oxygen, and 20 mtorr of molecular oxygen with helium as carrier gas at a total pressure of 2 torr. Concentration profiles of all species were measured by a molecular beam sampling