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Figure 1. Fe(phen)$_3$$^{2+}$ production during bromomalonic acid oxidation by Fe(phen)$_3$$^{3+}$. Solid line is the experiment, broken line is calculated from expression 3: 

$[\text{BMA}] = 6.25 \times 10^{-3} \text{ M}$; $[\text{Fe(phen)}_3^{3+}]_0 = 1.25 \times 10^{-4} \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.5 \text{ M}$ ($k_b = 3.65 \text{ M}^{-1}$). The following values were ascribed to the constants in (3): $k_1 = 10 \text{ M}^{-1} \text{ s}^{-1}$, $k_1/k_2 = 5 \times 10^5 \text{ M}^{-2}$.

Expression 3 with appropriate values for the rate constants provides a fairly good approximation to the observed kinetics of the acidity function $h_b$ instead of the proton concentration $[H^+]$ is reasonable at high concentrations of $\text{H}_2\text{SO}_4$ ($[\text{H}_2\text{SO}_4] > 0.1 \text{ M}$).

The lower limit for $k_2$ was also estimated: $k_1 > 1 \text{ M}^{-1} \text{ s}^{-1}$.

Littler and Sayce$^{11}$ mentioned the ferrin reduction by malonic acid as a first order-reaction in Fe(phen)$_3$$^{3+}$ concentration. If it is so, the reason for the difference in kinetics of these two similar reactions is still to be clarified.

The results show that the rate of the Fe(phen)$_3$$^{3+}$ reduction by BMA decreases very rapidly with the accumulation of the reduced form of the catalyst Fe(phen)$_3$$^{3+}$. The slowing down can be accounted for by the reverse reaction (eq -1). This is the most probable reason for the fact that in the ferroin-catalyzed oscillatory reaction the phase of catalyst reduction is much longer than that of catalyst oxidation, while in the cerium-catalyzed one the two phases are comparable.

These results can contribute to a better understanding of the oscillation mechanism and pattern formation in the ferroin-catalyzed Belousov–Zhabotinsky system. They should be taken into account when constructing a mathematical model of these phenomena.

Acknowledgment. I am much obliged to the reviewer who called my attention to the ref 11 and 12.

Registry No. Ferroin, 14708-99-7; bromomalonic acid, 600-31-7.

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Proton Magic Angle Spinning Nuclear Magnetic Resonance and Temperature Programmed Desorption Studies of Ammonia on the Acidity of the Framework Hydroxyl Groups in the Zeolite H–ZSM-5 and in H–Boralite

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The acidity of the framework hydroxyl groups of H–ZSM-5 and H–boralite is investigated by means of proton magic angle spinning NMR and temperature programmed desorption of NH$_3$ (NH$_3$-TPD). The acidity decreases on going from Si–OH–A, the Bronsted acidic site in H–ZSM-5, to Si–OH–B, the Bronsted acidic site in H–boralite, to Si–OH, the terminating hydroxyl group of the zeolite lattice (silanol group). The sequence is in agreement with the NH$_3$-TPD results.

Introduction

Knowledge of the acidity of the framework hydroxyl groups is of great importance in catalysis by zeolites. Several methods are used to determine the acidity of solids, e.g., temperature programmed desorption of NH$_3$ (NH$_3$-TPD), titration with Hammett indicators, infrared spectroscopy, or $^{13}$C NMR with the use of probe molecules. Recently, $^1$H magic angle spinning NMR (MAS NMR) has been applied to the study of hydroxyl groups in zeolites$^{6,7}$ and in silica gel.$^8$ Freude, Hunger, and Himmelblow$^{18}$ discussed the ferriin reduction by malonic acid as a first order-reaction in Fe(phen)$_3$$^{3+}$ concentration. If it is so, the reason for the difference in kinetics of these two similar reactions is still to be clarified.

The results show that the rate of the Fe(phen)$_3$$^{3+}$ reduction by BMA decreases very rapidly with the accumulation of the reduced form of the catalyst Fe(phen)$_3$$^{3+}$. The slowing down can be accounted for by the reverse reaction (eq -1). This is the most probable reason for the fact that in the ferroin-catalyzed oscillatory reaction the phase of catalyst reduction is much longer than that of catalyst oxidation, while in the cerium-catalyzed one the two phases are comparable.

These results can contribute to a better understanding of the oscillation mechanism and pattern formation in the ferroin-catalyzed Belousov–Zhabotinsky system. They should be taken into account when constructing a mathematical model of these phenomena.

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Pfeifer\(^4\) have shown for zeolites that the positions of the OH resonances in the NMR spectrum are related to the acidity of the proton. In this report, the acidity of H–ZSM-5 and of H–boralite is compared by application of \(^1\)H MAS NMR and NH\(_3\)-TPD.

Zeolite H–ZSM-5 was discovered by Mobil Oil and has potential applications in the synthesis of gasoline from alcohols.\(^3,10\) Boralites are crystalline borosilicates with zeolite-like structures. In our case boralite has a zeolite ZSM-5-like structure, but because of its composition it is not considered to be a zeolite.\(^11\)

The acidity can be defined as the residual charge of the hydrogen atom of the hydroxyl group or as the ease with which the proton can be dissociated (the Bronsted definition). The proton chemical shift is a measure of the screening of the proton nuclear magnetic moment by electrons and thus related to the proton acidity of the hydroxyl group. The more acidic the proton, the lower the resonance field.\(^14\) In solids like zeolites, the proton line widths can be large due to dipolar couplings of the proton to neighboring spins (\(^1\)H, \(^{29}\)Al, \(^{27}\)Al) and due to the anisotropy of the proton chemical shift. The proton line width, therefore, has to be reduced by solid-state NMR line narrowing techniques like multiple pulse sequences\(^15\) and/or magic angle spinning.\(^16\) Due to an apparent local mobility of the protons, in our case magic angle spinning alone was sufficient to eliminate all line broadening due to anisotropic interactions like the dipolar coupling and chemical shift.

After the physically adsorbed water molecules were dissolved, the resulting spectrum, as reported earlier,\(^6,7\) consists of two NMR lines. The low-field resonance signal is assigned to protons in Bronsted acidic sites (Si–OH–Al) and water molecules chemisorbed at these sites. The high-field resonance signal comes from protons of the silanol groups (Si–OH) and water molecules around these groups. By comparison of the chemical shifts of the resonance signals an acidity sequence can be derived for the structural hydroxyl groups in H–ZSM-5 and H–boralite.

On the basis of the simple electrostatic valence model of Pauling\(^17\) this acidity sequence is discussed.

**Experimental Section**

**Preparation of the Samples.** The ZSM-5 sample (010277) was prepared according to a general method described by a Mobil Oil patent.\(^18\) Synthesis and applications are described in recent literature.\(^19,20\) In the synthesis of H–boralite a mixture of 112.6 g of SiO\(_2\) (Aerosol 200 by Degussa) in 1011 mL of 20% tetrapropylammonium hydroxide (by Fluka) and of 23.4 g of H\(_3\)B\(_3\)O\(_3\) (by Fluka) was added to 789 g of H\(_2\)O was subjected to a hydrothermal treatment at 150 °C in a Hastelloy-C metal autoclave for 8 days. The obtained solid product was washed, dried, and calcined in air at 500 °C and used without further treatments for ion exchange. X-ray diffraction measurements confirmed the crystalline character of all samples, which exhibited the typical diffraction pattern of zeolite ZSM-5.\(^18\)

For the H–boralite sample the same symmetry as for ZSM-5 was found, but small differences in the unit cell dimensions exist. Chemical analyses of the samples yield the following compositions: H–ZSM-5 (010277), SiO\(_2\)/Al\(_2\)O\(_3\) = 102; Na\(_2\)O/Al\(_2\)O\(_3\) = 0.11; H–boralite, SiO\(_2\)/B\(_2\)O\(_3\) = 220; Na\(_2\)O/B\(_2\)O\(_3\) < 0.2.

**TPD Techniques.** NH\(_3\)-TPD measurements were carried out with a Perkin-Elmer TGS-2 thermobalance. Adsorption of NH\(_3\) on the samples was carried out at 50 °C with a 5 vol% NH\(_3\) in He flow. After saturation of the catalyst by NH\(_3\) the physisorbed material was removed by stripping with He at the adsorption temperature. The chemically adsorbed material was removed by increasing the temperature at a heating rate of 10 °C/min and the amount was determined gravimetrically. The results are presented in a differential mode. From the TPD results adsorption enthalpies can be calculated by the method of Cvetanović and Amenomiya.\(^23\) It will be clear, however, that the temperatures belonging to the peak maxima are representative of the adsorption enthalpy and, consequently, the acidity.

**Procedures of Dehydration and Hydration for NMR Measurements.** The procedures for dehydration and hydration of the samples were recently described.\(^7\)

**NMR Techniques.** The \(^1\)H NMR spectra were measured on a 180-MHz FT spectrometer.\(^24\) The samples were spun at the magic angle at frequencies up to 4 kHz in a cylindrical double air-bearing KEL-F spinner.\(^25\) The magic angle spinners were filled under an anhydrous nitrogen gas atmosphere in a glove box.

**Results and Discussion**

\(^1\)H MAS NMR of H–ZSM-5 and H–Boralite. An untreated H–ZSM-5 sample gives one resonance signal right at the free H\(_2\)O position due to the large amount of physically adsorbed water in the channels and at the outer surface of the zeolite. After the sample was dehydrated, a two-line NMR spectrum is observed (see Figure 1). As reported earlier,\(^7\) the low-field resonance signal...
at \(\sim 6\) ppm (relative to \(\text{Me}_2\text{Si}\)) is assigned to protons in Bronsted acidic sites (Si-OH-Al) and water molecules chemisorbed at these sites. The high-field resonance signal at \(\sim 2\) ppm comes from protons of the silanol groups (Si-OH) and water molecules around these groups.

The absolute and relative intensities of the two resonances, which depend on the amount of water adsorbed, are discussed in refs 7 and 9. Here we want to concentrate on the line positions, which show no dependence on the amount of adsorbed water. It is well-known from liquid solution studies\(^{(26)}\) and from wide-line NMR studies of other zeolite–water systems,\(^{(27)}\) Linde A and faujasites, that the protons of water adsorbed at an adsorption site and the proton of the adsorption site itself exchange very rapidly. The chemical shift of such a fast exchange group, \(\delta\), is given by\(^{(28)}\)

\[
\delta = \frac{2n}{2n+1} \delta_{\text{H}_2\text{O}} + \frac{1}{2n+1} \delta_{\text{ZOH}}
\]

with \(n\) the number of water molecules in the water cluster at the adsorption site, \(\delta_{\text{H}_2\text{O}}\) the chemical shift of free liquid water, and \(\delta_{\text{ZOH}}\) the chemical shift of the adsorption site alone. This clearly shows that in the presence of adsorption sites the water position (\(\delta\)) is shifted due to exchange with a proton with a different chemical shift (\(\delta_{\text{ZOH}}\)).

The sign of the shift, upfield or downfield, depends on whether \(\delta_{\text{ZOH}}\) is smaller than or greater than \(\delta_{\text{H}_2\text{O}}\). The low-field resonance due to protons of and water molecules adsorbed at Bronsted sites, being at low field relative to the resonance of free \(\text{H}_2\text{O}\), immediately makes clear that the resonance of the bare Bronsted site, which we never observed, must be at lower field than the resonance of free water. This is in contrast to the bare silanol group which should be found upfield from free water. This demonstrates that, due to its shift to higher field, silanol groups are considerably less acidic than Bronsted acidic sites, in agreement with other investigations.\(^{(29)}\) Proton magic angle spinning NMR thus provide a clue for the study of acidity in zeolites.

Possible exchange between Bronsted sites in the pores and silanol groups is not taken into account here. Fast exchange, at rates faster than the NMR time scale (\(\tau^{-1} \sim 700\) Hz), does not occur since otherwise one coalesced signal would be observed. Any slow exchange does not change the arguments.

Another zeolite-like system whose proton spectrum can be compared to that of H-ZSM-5 is H–boralite. An untreated H–boralite sample gives one resonance signal at the \(\text{H}_2\text{O}\) position, clearly due, as in the case of H-ZSM-5, to the physically adsorbed water in the channels and at the outer surface. Drying the sample reveals only one asymmetrical NMR signal consisting of at least two components. The high-field component at \(\sim 2\) ppm, by comparison with H–ZSM-5 and silicalite,\(^{(26)}\) can be attributed to the fast exchanging groups of protons of the water clusters at the silanol groups. After adsorbing a certain amount of water the low-field component at \(\sim 3.5\) ppm manifests itself more clearly (see Figure 1); this signal increases in intensity but does not shift as more water is adsorbed. The low-field resonance signal is due to, as in the case of H–ZSM-5, the group of exchanging protons of the water cluster, and the proton of the Bronsted acidic site of H–boralite (Si-OH–B). That the low-field resonance signal was not clearly observed after drying is probably caused by the high Si:B ratio (\(\sim 110\)) and the position of the line of the dehydrated Bronsted acidic site (vide infra).

If we compare the chemical shifts of the low- and high-field resonance signals of H–boralite with those of H–ZSM-5 (see Figure 1 and Figure 2 in which, schematically, the shifts of the low-field resonance signals of both solid catalysts are drawn), then it can be seen that the chemical shifts of the high-field resonance signals (silanol groups) are the same but that the chemical shift of the low-field resonance signal of H–boralite is shifted to higher field relative to the low-field resonance signal of H–ZSM-5 and to water.

Whatever the mechanism for the averaging of the chemical shift of the proton in the water cluster and the Bronsted acidic proton may be, simple exchange as assumed for eq 1 or a more complicated process, it is believed to be true for both H–ZSM-5 and H–boralite that the resonance line of these protons will lie between the resonance value for free \(\text{H}_2\text{O}\) and the resonance position of the dehydrated Bronsted proton. The Bronsted resonance line for partly hydrated H–ZSM-5 lies at lower field than that of free \(\text{H}_2\text{O}\), while the Bronsted line for partly hydrated H–boralite is found at a higher field than free \(\text{H}_2\text{O}\). Consequently, the Bronsted line in dehydrated H–boralite (Si-OH–B) must be found at a higher field than that of H–ZSM-5 (Si-OH–Al) (see Figure 2). This proves that (due to its shift to higher field) H–boralite is less acidic than H–ZSM-5. The exact nature of the line widths of the \(^1\text{H}\) NMR spectra will be dealt with in a future paper.

**TPD Measurements.** The results of the NH\(_3\)-TPD measurements for H–ZSM-5, H–boralite, and a crystalline silicalite are shown in Figure 3. It is clear from this figure that most NH\(_3\) desorbs at the same temperature for all three samples. However, at temperatures above 573 K still some NH\(_3\) is adsorbed on H–ZSM-5, in contrast to H–boralite and silicalite. This shows that in H–ZSM-5 sites are present which are more acidic than all sites in H–boralite. Because the difference between H–ZSM-5 and H–boralite consists of the Al and B Bronsted sites, this implies that the H–ZSM-5 Bronsted site is more acidic than the H–boralite Bronsted site. This confirms the results from MAS \(^1\text{H}\) NMR.

**Discussion.** As was concluded, the acidity of the hydroxyl groups decreases in the order Si–OH–Al, Si–OH–B, and SiOH. This means that the bond strength (Bronsted definition) of the O–H bond increases in the same order. This indicates that by
The bond strength of the 0-H bond of the Bronsted acidic site is then 1/4, appreciably lower than the bond strength of the O-H bond in a silanol group, in agreement with our measurements. The bond strength of the O-H bond of the Bronsted acidic site in H-boralite is, according to the same calculation, also 1/4. However, as can be seen from eq 5, the bond strength of the O-H in boralite would increase if the $S(\text{B-O})$ bond strength decreases. $^{17}$

Conclusions

From NMR studies and temperature programmed NH$_3$ desorption it is concluded that the Bronsted acidic site in H-ZSM-5 is more acidic than in H-boralite, while these sites in turn are more acidic than the silanol group. This acidity sequence can be understood by a simple electrostatic model.

Acknowledgment. We thank Mr. J. W. M. van Os for his skilful technical assistance, P. van Oeffelt (DSM) for his NH$_3$-TPD measurements, and Prof. dr. E. de Boer for critically reading the manuscript. K. F. M. G. J. Scholle gratefully acknowledges financial support by DSM, Geleen, The Netherlands.

Registry No. NH$_3$, 7664-41-7.


(31) K. F. M. G. J. Scholle and W. S. Veeman, manuscript in preparation.