

## $^{129}\text{Xe}$ Nuclear magnetic resonance study on a solid-state defect in HZSM-5 zeolite

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### Abstract

HZSM-5 and NaZSM-5 zeolites of various Si/Al ratios ranging from 20 to 130 have been characterized by  $^{129}\text{Xe}$  nuclear magnetic resonance (NMR) spectroscopy at 296 K, following evacuation at temperatures between 673 and 823 K. Increases in the aluminum content and evacuation temperature resulted in significant increases in the  $^{129}\text{Xe}$  NMR line width and chemical shift of xenon adsorbed on HZSM-5. Similarly, the electron spin resonance (ESR) signal at  $g=2.000\pm 0.005$  increased in intensity with increasing Al content or evacuation temperature. In the case of NaZSM-5, evacuation at high temperature did not affect the  $^{129}\text{Xe}$  NMR spectrum, and the ESR signal disappeared. These results are attributed to paramagnetic solid-state defects in HZSM-5 arising from the hydroxyl groups that bridge the Al and Si atoms in the zeolite framework.

**Keywords:**  $^{129}\text{Xe}$  nuclear magnetic resonance; ZSM-5 zeolite; Solid-state defect; Electron spin resonance of zeolite

### 1. Introduction

The chemical shift and line width in the  $^{129}\text{Xe}$  NMR spectrum of xenon adsorbed or entrapped within a microporous material is highly sensitive to the microporous environment surrounding the xenon atom [1,2]. Thus, the use of  $^{129}\text{Xe}$  NMR spectroscopy is widely applicable as a probe for the study of microporous materials such as silica, alumina, active carbons [3] and zeolites [4,5].

Recently,  $^{129}\text{Xe}$  NMR spectroscopy has been used to study various aspects of MFI zeolites. These studies have included modification of HZSM-5 by phosphorus [6], structuring of a

ZSM-5 phase during synthesis [7], surface properties of Al and Ga MFI zeolites synthesized in a non-alkaline medium [8], coke formation on HZSM-5 [9] and the effect of the Si/Al ratio on the chemical shift for HZSM-5 [10,11]. Some workers reported that a decrease in pressure resulted in a linear decrease in the  $^{129}\text{Xe}$  NMR chemical shift. Conversely, others reported that the pressure decrease resulted in a sharp increase in the chemical shift, particularly for HZSM-5 at pressures below 5 kPa [6,8,10]. Seo and Ryoo [6] speculated that the latter could be due to impurities or solid-state defects in the zeolite. Chen and co-workers [8,10] observed a similar change at low pressure when extra-framework Al and Ga species were present in the zeolite. Moreover, because of the high Si/Al ratios in MFI zeolites, the  $^{129}\text{Xe}$

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NMR chemical shift due to framework modification is influenced only to a small extent compared with the chemical shifts for other highly aluminous zeolites. The  $^{129}\text{Xe}$  NMR chemical shift and line width for MFI require more careful analysis than those of zeolites of higher aluminum content.

In the present work, we have focused our attention on the  $^{129}\text{Xe}$  NMR line broadenings and chemical shifts for HZSM-5 at low pressures. We have analyzed  $^{129}\text{Xe}$  NMR spectra of NaZSM-5 and HZSM-5 zeolites of various Si/Al ratios ranging from 20 to 130. The analysis was conducted after the samples were evacuated at temperatures between 673 and 823 K.

## 2. Experimental

ZSM-5 zeolites with various Si/Al ratios were synthesized using tetrapropylammonium bromide as a template [12]. Chemical analysis yielded Si/Al ratios of 20, 70 and 130. The zeolites were calcined in air at 773 K overnight and ion-exchanged with aqueous solutions of  $\text{NH}_4\text{Cl}$  and  $\text{NaCl}$  at room temperature (RT). The resulting NaZSM-5 and  $\text{NH}_4\text{ZSM-5}$  zeolites were washed with doubly distilled water and dried in a vacuum oven at RT. The zeolite samples were evacuated inside a xenon NMR cell [13] and an ESR tube while being heated to the maximum temperature (673, 773 or 823 K). The rate of heating was  $1.67 \text{ K min}^{-1}$  and the maximum temperature was maintained for 2 h under a nominal vacuum ranging from  $1 \cdot 10^{-3}$  to  $1 \cdot 10^{-4}$  kPa. Zeolite samples obtained from  $\text{NH}_4\text{ZSM-5}$  after this treatment are referred to as HZSM-5.

For  $^{129}\text{Xe}$  NMR spectroscopy, sample tubes containing evacuated zeolites were equilibrated with xenon gas (Matheson, 99.995%) under 0.67–53.3 kPa at 296 K. An NMR spectrum was taken at each xenon pressure with a Bruker AM 300 instrument operating at 83.0 MHz for  $^{129}\text{Xe}$  with a 1-s relaxation delay. The chemical shift was referenced to xenon gas extrapolated to zero pressure. The line width was determined by Lorentzian curve fitting. The ESR signal was measured at RT using a Varian E-4 instrument.

The  $^{129}\text{Xe}$  NMR and ESR spectra were also

taken after the evacuated NaZSM-5 and HZSM-5 zeolites were treated with  $\text{O}_2$  and  $\text{C}_2\text{H}_4$ . For treatment with  $\text{O}_2$ , the zeolites were equilibrated with 50-kPa  $\text{O}_2$  gas at 473 K for 2 h and subsequently evacuated for 1 h at RT. For treatment with  $\text{C}_2\text{H}_4$ , the zeolites were equilibrated with 1.3-kPa  $\text{C}_2\text{H}_4$  at RT and subsequently evacuated for 5 min under a nominal vacuum of  $1 \cdot 10^{-3}$  kPa.

## 3. Results

Typical  $^{129}\text{Xe}$  NMR spectra of NaZSM-5 and HZSM-5 are presented in Fig. 1. A single Lorentzian line was observed in each spectrum. In Fig. 2, the NMR line width is plotted against the xenon pressure. The NMR line width for HZSM-5 was broader than that for NaZSM-5 and increased sharply as the pressure decreased below 5 kPa. In contrast, the line width for NaZSM-5 was smaller than 200 Hz and depended very little on pressure. Moreover, the line width for HZSM-5 increased markedly after evacuation above 673 K, while the line width for NaZSM-5 was not affected. The excess line broadening disappeared completely after HZSM-5 was treated with  $\text{O}_2$ .

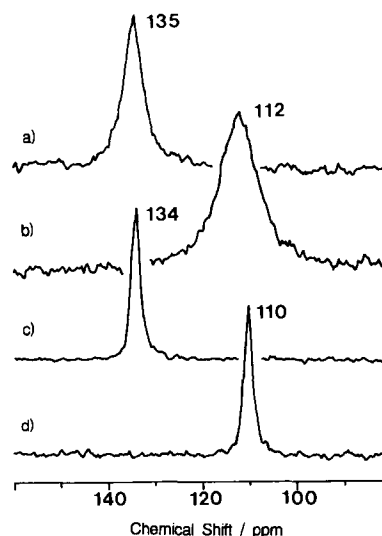


Fig. 1. Typical  $^{129}\text{Xe}$  NMR spectra of ZSM-5 zeolites equilibrated with xenon at 296 K: HZSM-5 of Si/Al=20 at (a) 53.3 and (b) 6.65 kPa; NaZSM-5 of Si/Al=20 at (c) 53.3 and (d) 6.65 kPa.

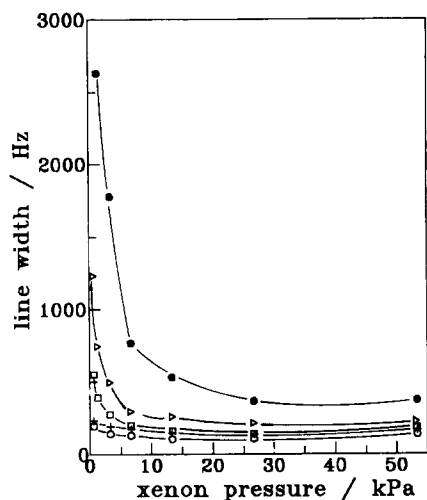


Fig. 2. Plots of  $^{129}\text{Xe}$  NMR line widths for ZSM-5 of Si/Al=70 against xenon pressure at 296 K:  $\square$ ,  $\triangle$  and  $\bullet$ , HZSM-5 evacuated at 673, 773 and 823 K, respectively; +, HZSM-5 evacuated at 773 K, after chemisorption of  $\text{O}_2$  at 473 K;  $\circ$ , NaZSM-5 evacuated at 773 K.

The  $^{129}\text{Xe}$  NMR chemical shifts for NaZSM-5 and HZSM-5 are compared in Fig. 3. The chemical shift for NaZSM-5 decreased monotonically with decreasing xenon pressure. In contrast, a minimum for the chemical shift was observed in the region

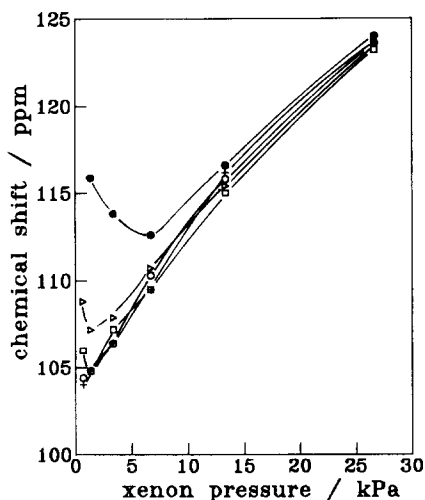


Fig. 3. Plots of  $^{129}\text{Xe}$  NMR chemical shifts for ZSM-5 of Si/Al=70 against xenon pressure at 296 K:  $\square$ ,  $\triangle$  and  $\bullet$ , HZSM-5 evacuated at 673, 773 and 823 K, respectively; +, HZSM-5 evacuated at 773 K, after chemisorption of  $\text{O}_2$  at 473 K;  $\circ$ , NaZSM-5 evacuated at 773 K.

3–7 kPa. The chemical shift for HZSM-5 sharply increased as the pressure decreased further. Thus, the chemical shift for HZSM-5 at low pressure was much larger than that for NaZSM-5. The difference in chemical shift between HZSM-5 and NaZSM-5 increased as the evacuation temperature increased. However, the chemical shift difference disappeared after HZSM-5 was treated with  $\text{O}_2$ . Thus, the chemical shift was affected by the same experimental factors as for line broadening. The  $^{129}\text{Xe}$  NMR line width and the chemical shift for HZSM-5 zeolites of various Si/Al ratios after evacuation at 773 K are displayed in Figs. 4 and 5, respectively. The NMR line width and chemical shift increased with Al content. Very similar to the treatment with  $\text{O}_2$ , the adsorption of  $\text{C}_2\text{H}_4$  resulted in decreases in the chemical shift and line width.

ESR spectra of ZSM-5 zeolites after evacuation are shown in Fig. 6. While a signal with  $g=2.000\pm 0.005$  can clearly be seen in the ESR spectrum of HZSM-5, the signal intensity for NaZSM-5 was negligible. Although the spin density was not measured from the ESR spectra, it was clear that the signal intensity increased with increasing evacuation temperature and Al content. The sample treatments with  $\text{O}_2$  and  $\text{C}_2\text{H}_4$  did not affect the ESR spectra.

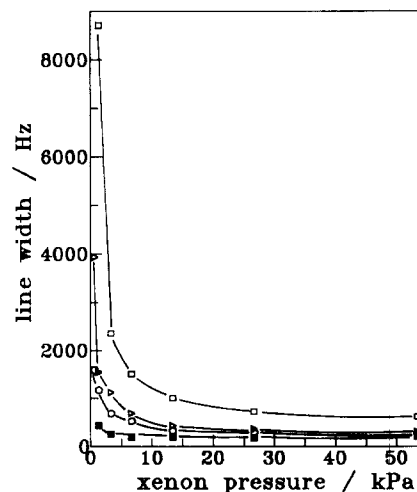


Fig. 4. Plots of  $^{129}\text{Xe}$  NMR line widths for HZSM-5 against xenon pressure at 296 K:  $\square$ , Si/Al=20;  $\triangle$ , Si/Al=70;  $\circ$ , Si/Al=130;  $\blacksquare$ , Si/Al=20, after adsorption of  $\text{C}_2\text{H}_4$  at RT. All samples were evacuated at 773 K.

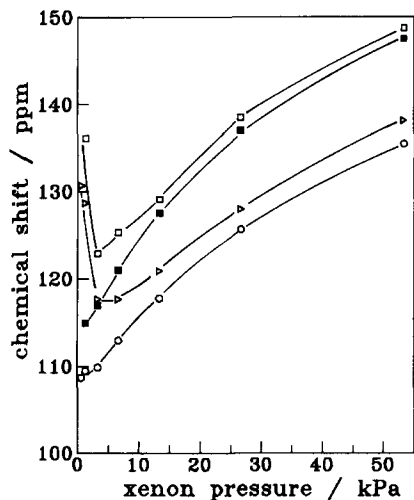


Fig. 5. Plots of  $^{129}\text{Xe}$  NMR chemical shifts for HZSM-5 against xenon pressure at 296 K:  $\square$ , Si/Al=20;  $\triangle$ , Si/Al=70;  $\circ$ , Si/Al=130;  $\blacksquare$ , Si/Al=20, after adsorption of  $\text{C}_2\text{H}_4$  at RT. All samples were evacuated at 773 K.

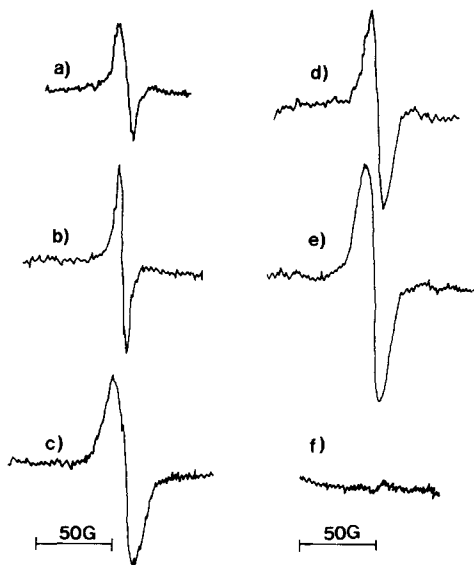


Fig. 6. ESR spectra for solid-state defects on ZSM-5 surface at 296 K: (a) HZSM-5 of Si/Al=70 evacuated at 773 K; (b) HZSM-5 of Si/Al=70 evacuated at 823 K; (c) HZSM-5 of Si/Al=20 evacuated at 773 K; (d) HZSM-5 of Si/Al=70 evacuated at 773 K, after chemisorption  $\text{O}_2$  at 473 K; (e) HZSM-5 of Si/Al=20 evacuated at 773 K, after adsorption of  $\text{C}_2\text{H}_4$ ; (f) NaZSM-5 of Si/Al=70 evacuated at 773 K.

#### 4. Discussion

Figs. 3 and 5 show that the chemical shift for HZSM-5 increases as the pressure decreases below 5 kPa. Similar changes in the  $^{129}\text{Xe}$  NMR chemical shift at low pressures have also been reported for NaY zeolites containing group 8 metal clusters and multivalent cations. The metal clusters include 1-nm Pt [14–16], Pd [17], Ru [18] and Ir [19] clusters located inside the supercages. The cation zeolites are NiNaY [20], CaY [21] and yttrium-NaX [22]. Recently, the dependence of the chemical shift on xenon pressure has been explained as due to a rapid xenon exchange between strong and weak adsorption sites [15,22]. The strong adsorption sites can be metal clusters or multivalent cations, while the weak adsorption sites are present over the aluminosilicate framework surface. The chemical shift  $\delta$  can then be written as:

$$\delta \approx \delta_{\text{S-Xe}} + \delta_{\text{Xe-Xe}} \\ = f_{\text{S}}\delta_{\text{SS-Xe}} + f_{\text{W}}\delta_{\text{WS-Xe}} + \delta_{\text{Xe-Xe}} \quad (1)$$

where  $\delta_{\text{S-Xe}}$  is the chemical shift component due to the interaction between Xe and the zeolite surface,  $\delta_{\text{Xe-Xe}}$  is the component of the chemical shift due to the Xe-Xe interaction,  $\delta_{\text{SS-Xe}}$  is the component of the chemical shift for the interaction between xenon and the strong adsorption site,  $\delta_{\text{WS-Xe}}$  is the component due to the interaction between Xe and the weak adsorption site,  $f_{\text{S}}$  is the probability of adsorption on the strong adsorption site, and  $f_{\text{W}}$  is the probability of adsorption on the weak adsorption site; it should be noted that  $f_{\text{S}} + f_{\text{W}} = 1$ .

At very low pressures, adsorption occurs selectively at strong adsorption sites. The interaction of the xenon with these sites leads to strong polarization and, consequently, the chemical shift increases. The number of strong adsorption sites is very small compared with the number of weak adsorption sites, which occupy most of the zeolite surface. Thus, strong adsorption sites become saturated with xenon, while the population of adsorbed xenon on the weak adsorption sites increases in a linear fashion with increasing xenon pressure [15,22]. Averaging of the chemical shift due to rapid exchange of xenon between strong and weak

adsorption sites is weighted progressively more towards the weak adsorption sites as the pressure is increased. This leads to a negative slope at low pressure in the chemical shift–pressure curve. For very high pressures, the xenon–xenon interaction term becomes important and therefore the chemical shift increases.

The NMR line width versus pressure curves as shown in Figs. 2 and 4 can be explained with an equation similar to Eq. 1 with the proper line width terms substituted for chemical shift terms. Strong adsorption of xenon on metal clusters and multivalent cations has been reported to cause very large  $^{129}\text{Xe}$  NMR line broadening in the Pt–NaY [15], Pd–NaY [17] and NiNaY [20] systems. There was little line broadening in the case of MgY, CaY [21] and yttrium–NaX [22] zeolites. Within HZSM-5 zeolite, there are no multivalent cations or metal clusters that can contribute to the line broadening, due to strong adsorption. Figs. 2 and 3 indicate that the adsorption site responsible for the line broadening has either a species that reacts with oxygen or, alternatively, one that chemisorbs oxygen at 473 K. The  $^{129}\text{Xe}$  NMR line broadening site in HZSM-5 also chemisorbed ethylene. The extra-framework aluminum species such as aluminum oxides and cations do not react with or chemisorb oxygen or ethylene under these experimental conditions.

ESR measurements were consistent with the effects shown in the  $^{129}\text{Xe}$  NMR spectra. Increasing Al content or sample evacuation temperatures led to an increase in electron spins in the HZSM-5 sample. In contrast, NaZSM-5 under the same experimental conditions did not give an ESR signal. Thus, electron spins are responsible for the line broadening and chemical shift in the  $^{129}\text{Xe}$  NMR spectra of HZSM-5 zeolite evacuated at high temperature. A mechanism has been proposed by Shih [23] for the formation of solid-state defects from Brønsted acid sites in HZSM-5 due to calcination in air at high temperature. It is believed that high-temperature evacuation of HZSM-5 can in a similar way lead to the formation of paramagnetic solid-state defects. The catalytic activity of HZSM-5 is known to be influenced by the dehydration temperature and aluminum content [24–26], and many catalytically active sites

were proposed to be related to solid-state defects [23].

It may be speculated that the solid-state defect sites would initiate free-radical chain reactions by chemisorbing reactants such as  $\text{O}_2$  and  $\text{C}_2\text{H}_4$ . This would lead to coke formation or participation in a catalytic reaction cycle. The ESR signals shown in Fig. 6, which were present after  $\text{O}_2$  and  $\text{C}_2\text{H}_4$  chemisorption, may be explained in this manner.

## 5. Conclusion

We have observed significant increases in the  $^{129}\text{Xe}$  NMR line width and chemical shift as the equilibrated xenon pressure decreased to below 5 kPa on HZSM-5 zeolites after evacuation at high temperatures above 673 K. Appearance of an ESR signal was also observed with the  $^{129}\text{Xe}$  NMR spectral change. This observation indicates the presence of a paramagnetic species that can adsorb xenon strongly on the zeolite surface. Since this paramagnetic effect increased with aluminum content in the case of HZSM-5 zeolites, but disappeared in the case of NaZSM-5, we conclude that a free-radical, solid-state defect can be generated from the hydroxyl group bonded to the framework Al and Si atoms when HZSM-5 is subject to dehydration at high temperature.

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