

Site Selective Line Broadening in Magic Angle Spinning ^{29}Si NMR of CuX Zeolite

Ja Hun Kwak and Ryong Ryoo*

Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Taeduk Science Town, Taejon, 305-701, Korea

Received: August 2, 1993; In Final Form: September 13, 1993*

The effect of a paramagnetic Cu^{2+} ion exchange on NMR line broadening was examined by using magic angle spinning ^{29}Si NMR spectroscopy. The NMR spectrum showed very selective, local line broadening effects for the Si atoms in the SiO_4 framework units, onto which the Cu^{2+} is thought to be exchanged. This effect was used to investigate the local ion-exchange site selectivity of Cu^{2+} over Na^+ , Zn^{2+} , Y^{3+} , and Ag^+ in X zeolites.

Introduction

High-resolution solid-state ^{29}Si NMR spectroscopy provides local information on SiO_4 tetrahedral units in zeolite frameworks.¹ The chemical shift for the Si atom of the Q_n [i.e., $\text{Si}(\text{OSi})_n(\text{OAl})_{4-n}$] framework unit differs significantly according to the number n , which ranges from 0 to 4.²⁻⁴ The Si/Al ordering in the zeolite framework can be measured by using relative intensities of the ^{29}Si NMR lines.^{2,5} The chemical shift can be affected by a cation exchange on the zeolite framework.⁶ However, this chemical shift effect is not sufficient for the investigation of local Si/Al ordering at the ion-exchange site. The local structure related to the ion-exchange selectivity may be obtained from the ^{29}Si NMR spectra, if we exchange a paramagnetic probe ion that can cause the ^{29}Si NMR line broadening selectivity at the ion-exchange site. From this point, we have measured ^{29}Si NMR spectrum of X zeolites against the degree of ion exchange of paramagnetic Cu^{2+} .

Experimental Section

High-purity NaX zeolite was prepared according to the procedure in the literature.⁷ The unit cell formula of the NaX zeolite was obtained as $\text{Na}_{80}[(\text{AlO}_2)_{80}(\text{SiO}_2)_{112}]$ by elemental analysis. Cu^{2+} ion was exchanged by stirring the NaX zeolite in aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich, 99%) overnight at room temperature (RT). The sample was filtered and thoroughly washed with doubly-distilled water. The ion exchange of Cu^{2+} in ammine form was performed in the same procedure by using concentrated ammonia solution instead of water. Samples containing Cu^{2+} and one of Zn^{2+} , Y^{3+} , and Ag^+ were obtained by the simultaneous ion exchange with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 (Shinyo, minimum 96%), $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Aldrich, 99.99%), and AgNO_3 (Inuishi, 99.8%). All samples were evacuated at RT before NMR measurements. The degree of ion exchange, i.e., percent Na^+ ion exchanged by others, was determined from chemical analysis using atomic absorption spectroscopy (Instrumental Analysis, Video 12) and is given by a number in parentheses for the sample notation. Sample notations AgX and ZnX mean that the ion-exchange level was maximized by repeating the ion-exchange treatment in large excess at least three times.

Solid-state ^{29}Si NMR spectra were obtained at 296 K using a Bruker AM-300 FT-NMR spectrometer with magic angle spinning unit. The operating frequency of ^{29}Si was 64.381 MHz, and the sample was spun at 3.5 kHz. The spectrum with Cu^{2+} ion was obtained with an acquisition of ca. 200 pulse transients, which was repeated with 5-s recycle delay and 3- μs pulse width. The recycle delay for NaX without Cu^{2+} was 20 s. The chemical shift was referenced with respect to the ^{29}Si signal of tetramethylsilane.

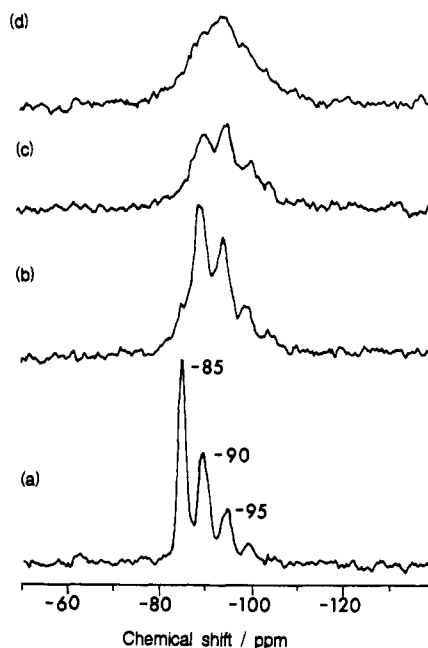


Figure 1. Solid-state ^{29}Si NMR spectra of CuNaX: (a) NaX, (b) Cu(12)NaX, (c) Cu(33)NaX, (d) Cu(59)NaX. The number in parentheses represents the degree of ion exchange.

Results and Discussion

Figure 1 displays a systematic change in ^{29}Si NMR spectrum of CuNaX against the degree (%) of Cu^{2+} ion exchange into NaX zeolite in aqueous media. Figure 1a was obtained from the starting NaX zeolites. This spectrum shows five well-resolved peaks at -85, -90, -95, -100, and -105 ppm, which can be assigned from $\text{Si}(\text{OAl})_4$, $\text{Si}(\text{OAl})_3(\text{OSi})_1$, $\text{Si}(\text{OAl})_2(\text{OSi})_2$, $\text{Si}(\text{OAl})_1(\text{OSi})_3$, and $\text{Si}(\text{OSi})_4$ tetrahedral units in the zeolite framework, respectively. A Si/Al ratio of 1.3 can be obtained from the relative peak intensities, and this result agrees with the chemical analysis within ± 0.1 . Therefore, the presence of nonframework Al can be neglected. Figure 1b was obtained after the ion exchange of 12% Na^+ with Cu^{2+} . The $\text{Si}(\text{OAl})_4$ peak intensity was decreased by the Cu^{2+} exchange, whereas the other peaks were not yet affected significantly. That is, the ^{29}Si NMR line broadening was selective to the $\text{Si}(\text{OAl})_4$ peak in this case. The chemical shift of the remaining peaks did not change significantly. Figure 1c shows that the other peaks became affected successively as the ion-exchange level was further increased. Eventually, all fine structure in the NMR spectrum disappeared as in Figure 1d. Such ^{29}Si NMR line broadening should be attributed to the paramagnetism of Cu^{2+} ion with an unpaired electron in the 3d orbital.

* Abstract published in *Advance ACS Abstracts*, October 1, 1993.

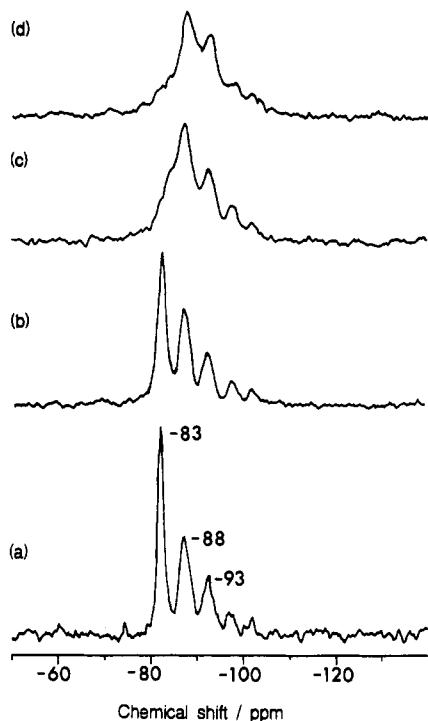


Figure 2. Solid-state ^{29}Si NMR spectra of CuAgX: (a) AgX, (b) Cu(9)AgX, (c) Cu(28)AgX, (d) Cu(10)Ag(50)NaX.

The selectivity in ^{29}Si NMR line broadening for Cu(12)NaX requires that the Cu^{2+} ion exchange was selective to a site which was near to $\text{Si}(\text{OAl})_4$, and the effect of paramagnetic line broadening was limited to within a short range not affecting the other sites. It will be interesting to discuss how much of the $\text{Si}(\text{OAl})_4$ peak intensity was affected by the above 12% ion exchange with Cu^{2+} . Figure 1a shows that the $\text{Si}(\text{OAl})_4$ peak intensity amounted to 40% of the total peak area before the ion exchange. The $\text{Si}(\text{OAl})_4$ peak intensity became negligible after the ion exchange of 12% Na^+ with Cu^{2+} . Correspondingly, the total peak intensity was decreased by the Cu^{2+} exchange. How did the ion exchange of only 12% Na^+ ion with Cu^{2+} affect so much the peak intensity? Let us compare Figures 1b and 2b. Figure 2b shows a ^{29}Si NMR spectrum obtained after ion exchange of 9% Ag^+ of AgX zeolite into Cu^{2+} . The decrease in $\text{Si}(\text{OAl})_4$ peak intensity for this Cu(9)AgX is considerably smaller than the corresponding decrease due to Cu^{2+} exchange into NaX. We obtain low-temperature NMR spectra for Cu(12)NaX. The $\text{Si}(\text{OAl})_4$ peak intensity was regained by about 50% at 243 K as compared with that at 296 K. This result indicates that the Cu^{2+} ion in zeolite underwent rapid exchange between several $\text{Si}(\text{OAl})_4$ sites within the NMR time scale. The Cu^{2+} exchange rate seemed faster in Cu(12)NaX, decreasing the NMR peak intensity to a much greater extent than in Cu(9)AgX. The change from spectra a through d of Figure 1 indicates that the Cu^{2+} ions become progressively exchanged onto $\text{Si}(\text{OAl})_3$, $\text{Si}(\text{OAl})_2$, and $\text{Si}(\text{OAl})_1$ with increasing ion-exchange level. The paramagnetic effect was spread all over the SiO_4 units, removing the entire fine structure under high Cu^{2+} loading. Thus, it is clear that the site preference of Cu^{2+} ion was $\text{Si}(\text{OAl})_4 > \text{Si}(\text{OAl})_3 > \text{Si}(\text{OAl})_2 > \text{etc.}$

The selective NMR line broadening can be useful for the study of the site selectivity of other cations as demonstrated in Figure 3. Figure 3a was obtained under simultaneous ion exchange of 10% Cu^{2+} and 10% Zn^{2+} into NaX zeolite. The spectrum is similar to Figure 1b for Cu(12)NaX. The Cu^{2+} ion seemed to remain at the $\text{Si}(\text{OAl})_4$ site when 10% Zn^{2+} ion was coexchanged. The $\text{Si}(\text{OAl})_4$ peak intensity was regained in Figure 3c,d, as the Zn^{2+} exchange level was successively increased under constant 10% Cu^{2+} exchange. In Figure 3c, the NMR lines for $\text{Si}(\text{OAl})_3$, $\text{Si}(\text{OAl})_2$, and $\text{Si}(\text{OAl})_1$ are as intense as those for the starting NaX zeolite. Most of the Cu^{2+} ions still seemed to be located

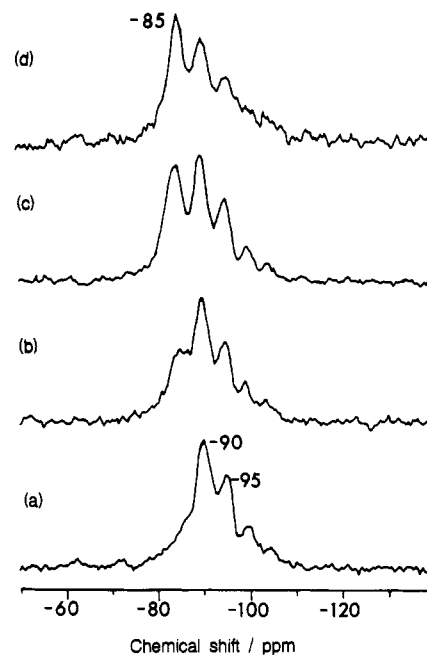


Figure 3. Solid-state ^{29}Si NMR spectra of CuZnNaX: (a) Cu(10)Zn(10)NaX, (b) Cu(10)Zn(30)NaX, (c) Cu(10)Zn(49)NaX, (d) Cu(10)-ZnX.

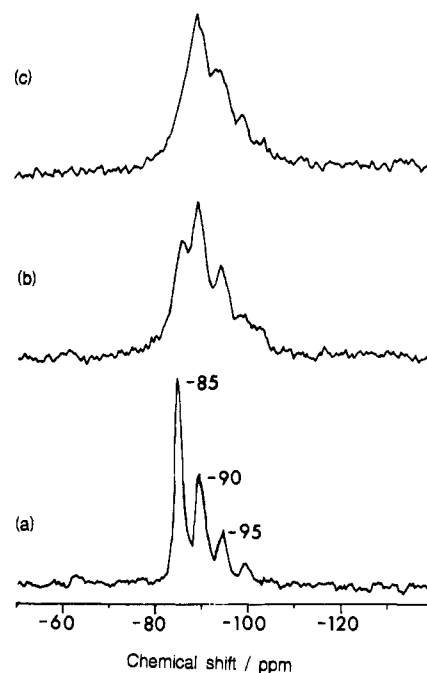


Figure 4. Solid-state ^{29}Si NMR spectra of CuNaX prepared in ammonia solution: (a) NaX, (b) Cu(9)NaX, (c) Cu(33)NaX.

at the $\text{Si}(\text{OAl})_4$ site. Then, why did the $\text{Si}(\text{OAl})_4$ peak intensity increase from spectra a to b of Figure 3? Much more work is required to answer this question, but it may be speculated that the $\text{Si}(\text{OAl})_4$ peak intensity can be regained if the simultaneously introduced Zn^{2+} can inhibit rapid exchange of Cu^{2+} between $\text{Si}(\text{OAl})_4$. This is similar to the explanation given for the difference between Figures 1b and 2b. Clearly, many of the Cu^{2+} ions located at the $\text{Si}(\text{OAl})_3$ and $\text{Si}(\text{OAl})_2$ sites caused the line broadening at these sites in Figure 3d. Similar experiments were performed with Y^{3+} instead of Zn^{2+} , and the $\text{Si}(\text{OAl})_4$ peak intensity was regained more easily in this case. This suggests that the trivalent Y^{3+} has higher selectivity toward the $\text{Si}(\text{OAl})_4$ site than the Cu^{2+} does.

The ion exchange of Cu^{2+} in ammonia solution resulted in similar line broadening as shown in Figure 4. However, the site selectivity was decreased as compared to the case of Figure 1.

The NMR spectra were changed into the same results as Figure 1, when the samples were rehydrated after evacuation at 400 °C. Thus, the binding selectivity of the ammine complex was clearly smaller than the aqueous form. The selectivity difference between the aqueous and ammine forms can be due to differences in the ionic structure and mobility. For example, it can be speculated that the bulky $\text{Cu}(\text{NH}_3)_4^{2+}$ is not easily accessible to the ion-exchange sites in sodalite cages and hexagonal prisms that may have strong affinity with this ion.

In conclusion, the selective ^{29}Si NMR line broadening due to Cu^{2+} in this study suggests that such an NMR technique using paramagnetic ion can be very useful for the investigation of local Si/Al ordering at the ion-exchange site in zeolites.

References and Notes

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