EXAFS Investigation of Pentasil-Structured Gallium-Containing Metallosilicates

Kiyomi Okabe, Nobuyuki Matsubayashi,* Kazuhiro Sayama, Hironori Arakawa, and Akio Nishijima
Surface Chemistry Division, National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305

(Received January 28, 1991)

Synopsis. Pentasil-structured bimetallosilicates were prepared by adding Ga and Fe (or Sr) salts simultaneously during the hydrothermal synthesis of a pentasil silicate, and local structures around Ga were directly elucidated by means of EXAFS for the first time. It was found that Fe and Ga independently substituted the silicate framework, and that the local structure around Sr was the same as that in Sr^{2+}-exchanged gallosilicate.

It was reported that tectosilicate frameworks are substituted by such elements as B, Be, Al, Fe, Ga, Ge, Cr, P, and Mg.[1] Among these elements, B, Al, Fe, and Ga are most frequently used for preparing metallosilicate catalysts, since the acidity of the catalysts can be altered by the substitution. Pentasil metallosilicates, thus prepared, have a unique channel structure, and the framework metals are atomically dispersed. These characteristics provide long catalytic life as well as high activity in the conversion of methanol to hydrocarbons.[2] Selectivity is often improved by additives during the hydrothermal synthesis of the silicates.[3] However, interaction between the second metal and the metal in the framework of the silicates is not well-characterized at the present time. It is of great importance to elucidate the interaction, since the interaction may give rise to a change in electronic states of the active sites, improving the catalytic property. The purpose of the present investigation is to clarify the micro-structure around Ga in Ga-containing bimetallosilicates and to show the intermetallic interaction between Ga and the second metal by means of EXAFS. In the present investigation, Fe and Sr were chosen as the second metals, since (a) the former is typical of an isomorphous substitutional element and the latter is non-substitutional, as mentioned above, and (b) both are catalytically important additives and a large amount of data has been accumulated on their ability to modify the acidity of catalysts.[4]

Experimental

Colloidal silica, gallic nitrate (and/or iron(III) nitrate), tetrapropylammonium bromide (TPABr), sodium hydroxide, and distilled water were mixed together to form a metallosilicate (M-silicate; M=Ga, Fe) gel having the following composition; SiO_2/Ga_2O_3 (and/or Fe_2O_3)=200, SiO_2/TPABr=10, SiO_2/OH=10. The gel was crystallized by autoclaving at 433 K. Some of the crystalline metallosilicates were treated with 0.1 mol dm^{-3} aqueous solutions of $SrCl_2$ or $Ga(NO_3)_3$ at 373 K after calcination at 773 K, and the Na^+ of the pentasil silicates was replaced by Sr^{2+} or Ga^{3+}. Sr-containing gallosilicate was prepared by adding strontium acetate (Sr/Ga=10) during the hydrothermal synthesis of gallosilicate. The K-edge EXAFS spectra of Ga, Sr, and Fe were measured at the Photon Factory (BL-10B and BL-7C) of the National Laboratory for High Energy Physics. In Fourier transforms of the EXAFS data, the phase shifts due to an absorbing atom and backscattering atoms were corrected using parameters calculated by Teo and Lee[5] for M–O (M=Ga, Sr, Fe). Furthermore, the distances were corrected using the results for standard samples (Ga_2O_3, SrO, and Fe_2O_3).

Results and Discussion

Figure 1 shows the Fourier transforms of Ga K-edge EXAFS of (a) Ga_2O_3 and (b—e) gallosilicates at the various stages of the hydrothermal reaction. The profile of the gel mixture at an initial stage (b) was quite different from that of Ga_2O_3 (a). The peaks at 1.9 and 3.2 Å of Ga_2O_3 are assigned to Ga–O and Ga–O–Ga, respectively. The latter peak was not found in the spectra of the gallosilicates (b—e). The profiles of the silicates were almost unchanged during the hydrothermal reaction. The peaks at 3.1 and 3.5 Å may correspond to Ga–O–Si distances, as assigned previously.[6] The fact that the second neighboring atoms on Ga are

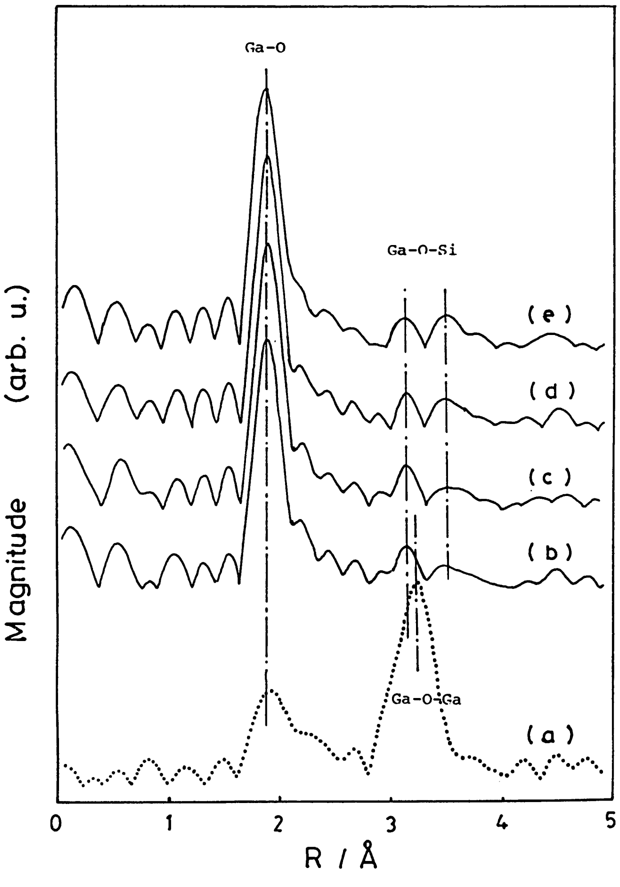

Fig. 1. Fourier transforms of Ga K-edge EXAFS with phase-shift correction of (a) Ga_2O_3, and gallosilicates after hydrothermal reaction of (b) 0 h, (c) 2 h, (d) 2.5 h, and (e) 6 h.

not Ga but Si indicates that Ga is highly dispersed in the silicate, even at the very beginning of the hydrothermal reaction. The atomic isolation of the metal in the silica matrix is different from the previous case of ferrisilicate, where FeO(OH) was formed in the starting gel.⁶⁾ The identical peak positions in the EXAFS profiles between the amorphous and crystalline phases strongly suggest that the micro-structure around Ga was formed in a very early stage of the hydrothermal reaction without the formation of an oxide or hydroxide of Ga, and that the local environment around Ga was almost unchanged throughout the hydrothermal reaction.

However, the relative intensity of the peaks at 3.5 Å increased and that at 3.1 Å decreased slightly with hydrothermal reaction time, as illustrated in Fig. 2. The change in XRD intensity at a spacing *d*(501) of the silicates (△) indicates that the silicate bulk was crystallized during a short period of time after a hydrothermal reaction time of 2 h. These results suggest that the peaks at 3.1 Å correspond to the Ga–O–Si distance in an amorphous silicate and the ones at 3.5 Å to that of the pentasil structure, and that the regularity of the micro-structure around Ga in the pentasil framework increased with time.

Figure 3 shows the Fourier transforms of Ga K-edge EXAFS of (a) Ga_2O_3, (b) Ga^{3+}-exchanged Fe-silicate, (c) Fe, Ga-bimetallosilicate, (d) Sr-containing Ga-silicate, and (e) pentasil structured Sr^{2+}-exchanged Ga-silicate.

The peak positions of (b) are different from those of Ga_2O_3 (a) or Ga-silicate (Fig. 1), implying that most of the Ga of (b) was in the form of counter cations to acid sites caused by the framework Fe. The peak at 3.0 Å of the silicate corresponds to the distance to the second neighboring atoms on Ga. The dissimilarity of the profiles suggests that the peak may correspond to the Ga^{3+}–O–Fe distance, since a peak of the same distance was also found in the Fourier transform of Fe K-edge EXAFS of Ga^{3+}-exchanged Fe-silicate. A weaker peak was found at 3.45 Å in profile (b) in Fig. 3. The relative peak intensity depends on many factors, the atomic weight of the adjacent atoms being one of them. By simply assuming that the atomic weight corresponding to the peak at 3.45 Å is about half that of the peak at 3.0 Å and that the other factors are the same between these two peaks, the weak peak can be explained in terms of the Ga–O–M distance. Si may be the most appropriate candidate for the M element, since the relative atomic weight ratio of Si/Fe is 0.5 and the distance derived from the peak position is similar to the Ga–O–Si distance in crystalline gallosilicate, as mentioned above. Thus, the peaks at 3.0 and 3.45 Å may be assigned to the Ga^{3+}–O–Fe and Ga^{3+}–O–Si distances, respectively.

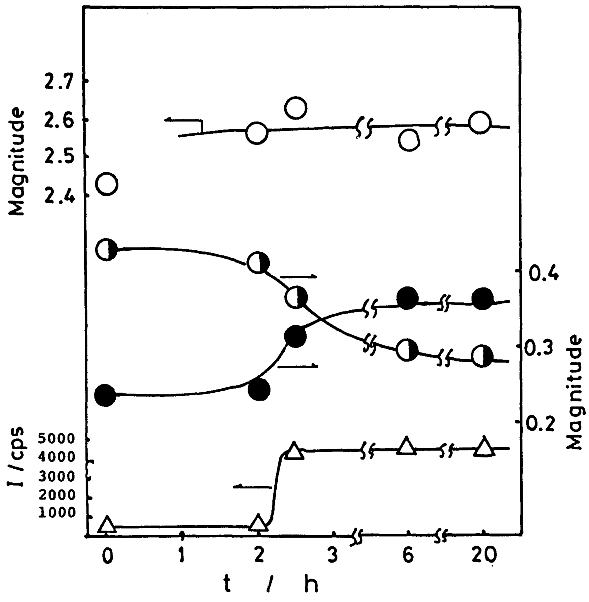

Fig. 2. Changes in peak intensities at 1.9 Å (○), 3.1 Å (◑) and 3.5 Å (●) of Fig. 1, and in XRD peak intensities at 2*θ*=23.2° (△) with hydrothermal reaction time.

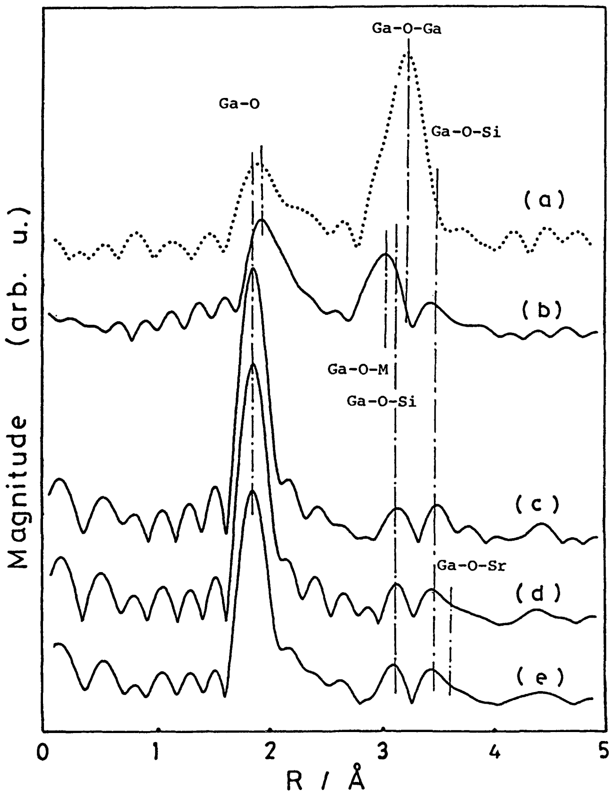

Fig. 3. Fourier transforms of Ga K-edge EXAFS, with phase-shift correction, of (a) Ga_2O_3, (b) Ga^{3+}-exchanged ferrisilicate, (c) Fe,Ga-bimetallosilicate, (d) Sr-containing gallosilicate, and (e) Sr^{2+}-exchanged gallosilicate.

The Ga–O distance in (c) is 1.9 Å, and is shorter than that in (b) by 0.1 Å. The profile of (c) in the range of 3.0—3.5 Å is also different from that of (b), and exactly the same as that of Ga-silicate. The peaks at 3.1 and 3.5 Å of Ga-silicate were both assigned to Ga–O–Si, as described above. The fact that no other peaks of Ga–O–M (M=Ga, Fe) are found in (c) suggests that Ga and Fe are atomically and independently dispersed in the silicate crystals without mutual interaction.

The profile of (d) is the same as (e), indicating that the local structures around Ga are similar to each other. The profiles are also similar to that of Ga-silicate (Fig.

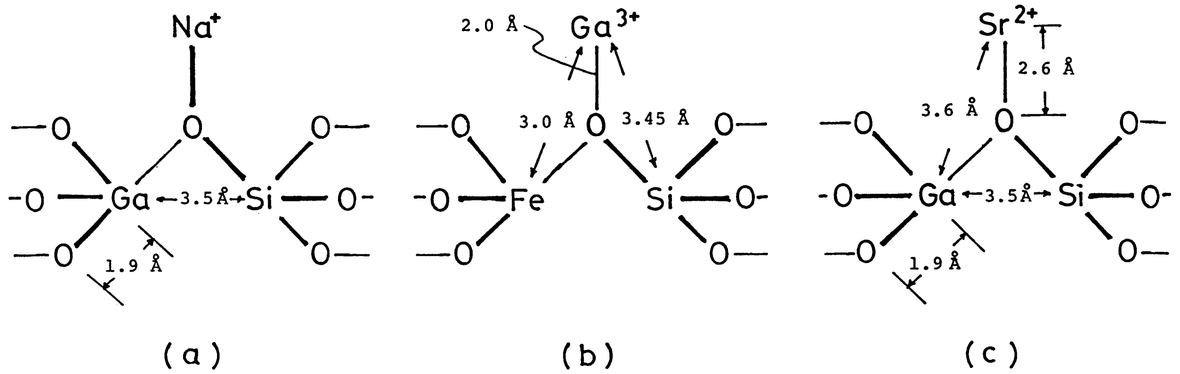

Fig. 5. Intermetallic distances determined by EXAFS of (a) gallosilicate, (b) Ga^{3+}-exchanged ferrisilicate, and (c) pentasil-structured Sr-containing gallosilicate.

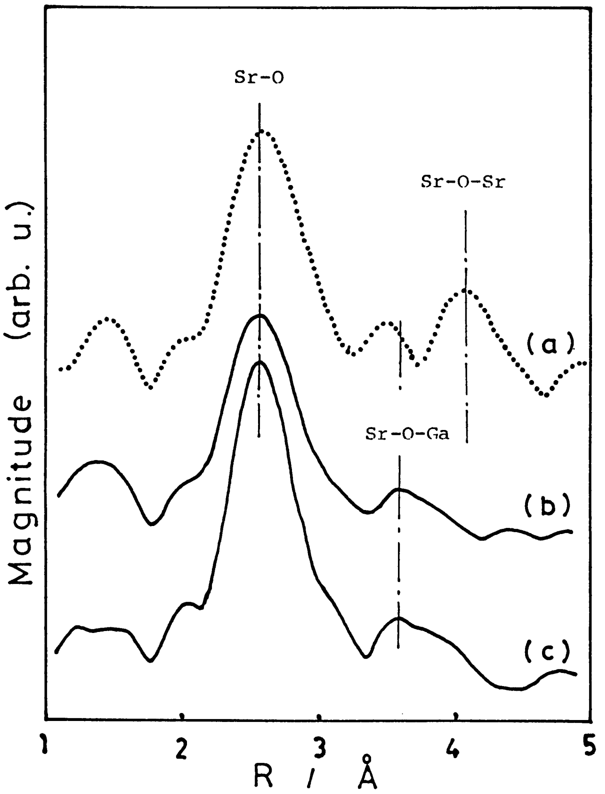

Fig. 4. Fourier transforms of Sr K-edge EXAFS, with phase-shift correction, of (a) SrO, (b) Sr-containing gallosilicate, and (c) Sr^{2+}-exchanged gallosilicate.

1), except for the peak broadening at 3.5—3.6 Å. It is well known that framework Ga gives rise to an acid site, and that Sr of (e) is in the form of an extra-framework cation attached to this site. Therefore, the broadening of the peak suggests that it actually consists of two peaks, Ga–O–Si (3.5 Å) and Ga–O–Sr^{2+} (3.6 Å). The latter peak was also found in the Fourier transforms of Sr K-edge EXAFS of Sr^{2+}-exchanged Ga-silicate and Sr-containing Ga-silicate, as depicted in Fig. 4. The similarity between the profiles of Sr^{2+}-exchanged Ga-silicate and Sr-containing Ga-silicate implies that most of Sr in the latter are not contained in the silica matrix, but are in extra-framework ion-exchanging sites.

In conclusion, intermetallic distances of pentasil-structured bimetallosilicates were directly and precisely determined by means of EXAFS, providing the following information on interactions between the metals:

(1) The micro-structure around Ga of gallosilicate was formed in a very early stage of the hydrothermal reaction, before bulk crystallization, without the formation of an oxide or hydroxide of Ga.

(2) In the crystallization of Fe, Ga-bimetallosilicate, no interactions between Fe and Ga were found structurally, and the silicate framework was substituted by either metal independently.

(3) The micro-structure around Sr in Sr-containing gallosilicate was similar to that of Sr^{2+}-exchanged silicate, and Sr was in an extra-framework ion-exchanging site.

It is believed that precise control of the interactions between metals in metallosilicates is prerequisite for improving the catalytic property. To accomplish this control, a large amount of data on interactions must be accumulated. We have found EXAFS to be a very powerful tool for clarifying the interaction from a structural point of view at the atomic level. More detailed structural data will be produced with further investigations by EXAFS.

References

1) R. M. Barrer, "Hydrothermal Chemistry of Zeolites," Academic Press, London (1982), p. 251.

2) T. Inui, O. Yamase, K. Fukuda, A. Itoh, J. Tarumoto, N. Morinaga, T. Hagiwara, and Y. Takegami, 8th International Congress on Catalysts, Berlin, 1984, Vol. 3, p. 569.

3) H. Okado, H. Shoji, K. Kawamura, Y. Shiomi, K. Fujisawa, H. Hagiwara, and H. Takaya, *Nippon Kagakukaishi,* **1987**, 962.

4) H. Hagiwara, K. Kawamura, S. Ikai, F. Mizuno, and H. Okado, "Progress in C_1 Chemistry in Japan," Kodansha, Tokyo (1989), p. 331.

5) B. K. Teo and P. A. Lee, *J. Am. Chem. Soc.,* **101**, 2815 (1979).

6) K. Okabe, N. Matsubayashi, H. Shimada, H. Hagiwara, and A. Nishijima, *Chem. Lett.,* **1990**, 955.