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THERMAL STABILITY OF [B]ZSM-5 MOLECULAR SIEVE

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Abstract—The thermal stability of [B]ZSM-5 (boronsilicalite) has been examined by IR, XRD, ^{11}B MAS NMR and XPS techniques. [B]ZSM-5 and amorphous borosilicate were converted to α-cristobalite at high temperatures (=750C). However, Na-free amorphous borosilicate was not converted to α-cristobalite at 750C. Therefore, the presence of Na^+ ions in [B]ZSM-5 would determine whether this transition occurred or not. When the phase transition to α-cristobalite occurred, most of B atoms tetrahedrally coordinated were released from the ZSM-5 structure and migrated to the exterior surface as a boron compound having trigonal BO_3 units and oxidation states of 3.

INTRODUCTION

Isomorphous substitution of various heteroatoms instead of Al atoms in the ZSM-5 structure has drawn a considerable interest recently. [B]ZSM-5, one of the ZSM-5 analogues, has been reported to have catalytic activity different from [Al]ZSM-5 for a number of acid-catalyzed reactions [1]. The fact that the catalytic activity of [B]ZSM-5 is due mainly, if not entirely, to the trace amounts of B atoms in the ZSM-5 structure has been confirmed by solid state NMR [2-4] and X-ray diffraction studies [5, 6]. However, the structural changes including the coordination of B atoms in the ZSM-5 structure remained unknown when [B]ZSM-5 was heated at high temperatures. In this paper, we present the details of structural changes of [B]ZSM-5 at high temperatures, which are investigated with IR, powder X-ray diffraction, ^{11}B magic angle spinning NMR, and X-ray photo-electron spectroscopy.

EXPERIMENTAL

[B]ZSM-5 was prepared by hydrothermal crystallization at 150C for 3 days from a mixture containing colloidal silica (SiO_2 40 wt%), boric acid, NaOH and tetrapropylammonium bromide (TPABr) according to the method of Howden [7] and Woo et al. [8]. The SiO_2/B_2O_3 and SiO_2/Na_2O mole ratios of the reaction mixture were 9.1 and 10.5, respectively. The final pH of reaction mixture was 10.4. Amorphous borosilicates were prepared under the same preparation condition as that of [B]ZSM-5 in the absence of TPABr or NaOH. Elemental analyses were done with atomic absorption spectroscopy. X-ray diffraction patterns were taken on a Rigaku D/Max II-A diffractometer using Ni-filtered Cu Kα radiation. IR spectra were recorded with an Analect 6160 Fourier Transformed Infrared Spectrophotometer. The ^{11}B NMR spectra were obtained using a Bruker AM-200 high resolution NMR spectrometer operating at a field of 4.7 T with a standard MAS probe. MAS was at 3.8 kHz using conical Delrin rotors. ^{11}B NMR measurements were carried out on fully hydrated samples which had been kept in a desiccator for 48 h saturated with NH_4Cl aqueous solution. The chemical shifts were determined from BF_3OEt_2 used as an external reference. The XPS measurements were carried out using a ESCA spectrometer (Model PHI 550, Perkin-Elmer). Monochromatic Mg Kα X-ray radiation (1253.6 eV) was used. The pressure in the analyzer chamber was 10^{-9} torr and the analyzer pass energy was 10 eV. The C(1s) (284.3 eV) line from the carbon impurity in [B]ZSM-5 was used as an internal standard to correct a shift in binding energy due to a charging effect (see Table 1). The correction factor was subtracted from the observed binding energies to compensate a charging effect.

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RESULTS AND DISCUSSIONS

1. Phase transition of [B]ZSM-5 and amorphous borosilicate

Elemental analysis showed that the actual mole ratios of SiO_2/B_2O_3 and SiO_2/Na_2O in the [B]ZSM-5 were 60.0 and 63.9, respectively. IR spectrum [Fig. 1 (a)] and XRD pattern [Fig. 2(a)] of [B]ZSM-5 as synthesized were the same as those of ZSM-5. When TPABr or NaOH was not added to the reaction mixture, amorphous borosilicate was prepared instead of [B]ZSM-5. However, for the amorphous borosilicate prepared in the absence of NaOH, small amount of crystalline ZSM-5 phase was found as an impurity in the XRD pattern of corresponding sample [Fig. 2(b)].

It was reported that [Al]ZSM-5 ($SiO_2/Na_2O=50.6$) was thermally stable enough to keep the structure unchanged up to 930°C [9]. Howden [7] reported that the boron counterpart of [B]ZSM-5 ($SiO_2/Na_2O=109.9$) was converted to cristobalite at temperatures above 700°C. However, Beyer[10] reported that Na-free [B] ZSM-5 showed the characteristic XRD pattern of the ZSM-5 structure even after calcination at 1000°C. Fig. 1 (a) and (b) indicate that the [B]ZSM-5 ($SiO_2/Na_2O=63.9$) calcined below 600°C shows the characteristic IR and XRD patterns of the ZSM-5 structure. When [B]ZSM-5 was calcined at 750°C, two typical bands of the ZSM-5 at 453 and 561 cm^{-1} disappeared and two new bands at 504 and 622 cm^{-1} appeared [Fig. 1 (c)]. And the IR spectrum was nearly same as that of SiO_2 quartz powder calcined at 1500°C which had the structure of cristobalite [11]. Therefore we can conclude that [B]ZSM-5 is converted to cristobalite at 750°C.

Such a phase transition was also observed for the amorphous borosilicate prepared in the absence of TPABr.

Elemental analysis showed that the mole ratio of SiO_2/Na_2O in the prepared amorphous borosilicate was 50.9. The IR spectra of amorphous borosilicates are shown in Fig. 3(b) and (d). When the amorphous borosilicate was calcined at 750°C, a new IR band appeared at 622 cm^{-1} and an IR band at 475 cm^{-1} was shifted to 486 cm^{-1} [Fig. 3(d)]. And by the comparison of Fig. 3(d) with Fig. 1(d), it was known that amorphous borosilicate containing Na^+ ion was converted to cristobalite at 750°C.

However, Na-free amorphous borosilicate prepared in the absence of NaOH was not converted to cristobalite at 750°C. This was evidenced by the fact that there were no significant changes in the IR spectrum before and after calcination at 750°C [see Fig. 3(a) and (c)]. And most of Na-free amorphous borosilicate was still remained as an amorphous phase even after calcination at 1000°C. Scherer studied crystal growth rates of the Na_2O-SiO_2 glasses for the different SiO_2/Na_2O mole ratios in the temperatures between 500°C and 1500°C. And he reported that the temperature at which Na_2O-SiO_2 glass crystallized into cristobalite increased from 650°C to 700°C as the mole ratio of SiO_2/Na_2O increased from 5.7 to 65.7 [12]. Considering the result of Na_2O-SiO_2 glass, it is believed that the presence of Na^+ ion is the major factor for the phase transition of [B]ZSM-5 and amorphous borosilicate to cristobalite.

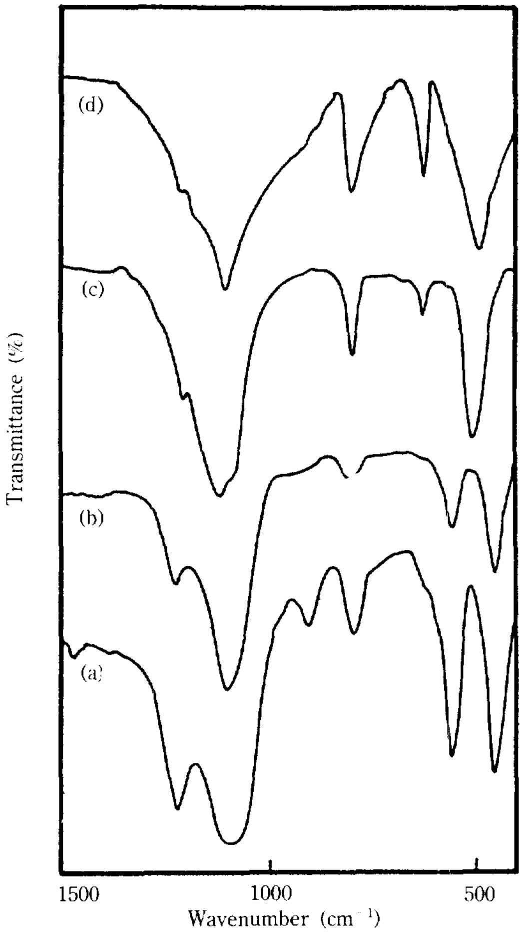

Fig. 1. Infrared spectra of [B]ZSM-5 (a) as synthesized, (b) calcined at 600°C, (c) calcined at 750°C, and (d) SiO_2 quartz powder calcined at 1500°C (cristobalite).

The transition temperature (=750°C) of [B]ZSM-5 is lower than that (>950°C) of [Al]ZSM-5, although the Na contents of [B]ZSM-5($SiO_2/Na_2O=63.9$) is less

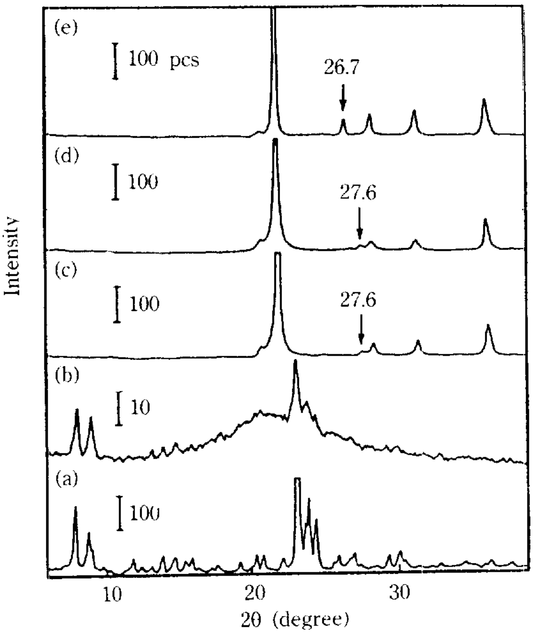

Fig. 2. XRD patterns of (a) [B]ZSM-5 as synthesized (SiO_2/Na_2O=63.9), (b) Na-free amorphous borosilicate calcined at 750℃, (c) sample of (a) calcined at 750℃, (d) amorphous borosilicate (SiO_2/Na_2O =50.9) calcined at 750℃, (e) SiO_2 quartz powder calcined at 1500℃ (α-cristobalite).

than that of [Al]ZSM-5(SiO_2/Na_2O=50.6)[9]. Therefore, it seems that the extraction of B atoms from the tetrahedral sites of the ZSM-5 structure is easier than that of Al atoms.

Other evidences for phase transition were obtained from XRD data as shown in Fig. 2. Fig. 2(c), (d), and (e) showed that [B]ZSM-5 and the amorphous borosilicate (SiO_2/Na_2O=50.9) calcined at 750℃ had the similar XRD patterns as that of SiO_2 quartz powder calcined at 1500℃(α-cristobalite)[11]. From the XRD data, we knew that [B]ZSM-5 and amorphous borosilicate calcined at 750℃ were converted to α-cristobalite. However, Na-free amorphous borosilicate was not converted to α-cristobalite after calcination at 750℃, because its XRD patterns as shown in Fig. 2(b) is completely different from that of α-cristobalite as shown in Fig. 2 (e).

A small peak was observed at 2θ=27.6℃ in XRD patterns of Fig. 2(c) and (d), which was not found in XRD patterns of α-cristobalite. It was reported that crystalline boron oxide did not have any strong peak at 2θ=27.6℃ except B_2O_3 having cubic symmetry [13]. Therefore, this peak can be assigned to the strongest peak of B_2O_3 having cubic symmetry. When [B] ZSM-5 and amorphous borosilicate are calcined at 750 ℃, B_2O_3 can be produced by the reaction of oxygen with boron atoms from the tetrahedral sites of the ZSM-5 structure.

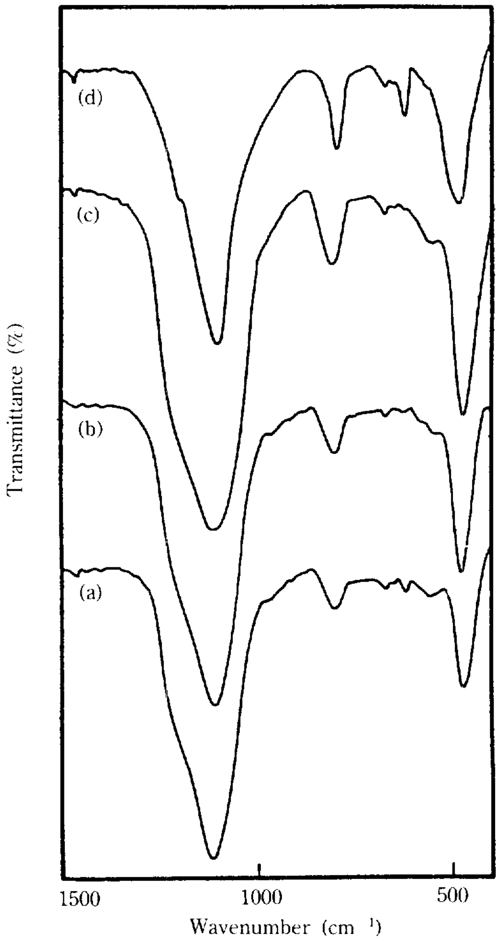

Fig. 3. Infrared spectra of (a) Na-free amorphous borosilicate, (b) amorphous borosilicate (SiO_2/Na_2O= 50.9), (c) sample of (a) calcined at 750℃, and (d) sample of (b) calcined at 750℃.

2. Coordination of B atoms after phase transition

High resolution solid state magic angle spinning ^{27}Al-, ^{29}Si- and ^{11}B NMR is the most powerful technique for the determination of the coordination state of atoms in zeolites. To know the coordination state of B atoms, ^{11}B NMR was used. The NMR band of B atoms tetrahedrally coordinated to oxygen atoms shifted from the band of BF_3OEt_2 in the range between −3 and 2 ppm[14]. This band was generally narrow and symmetrical in shape, bacause of the very small quad-

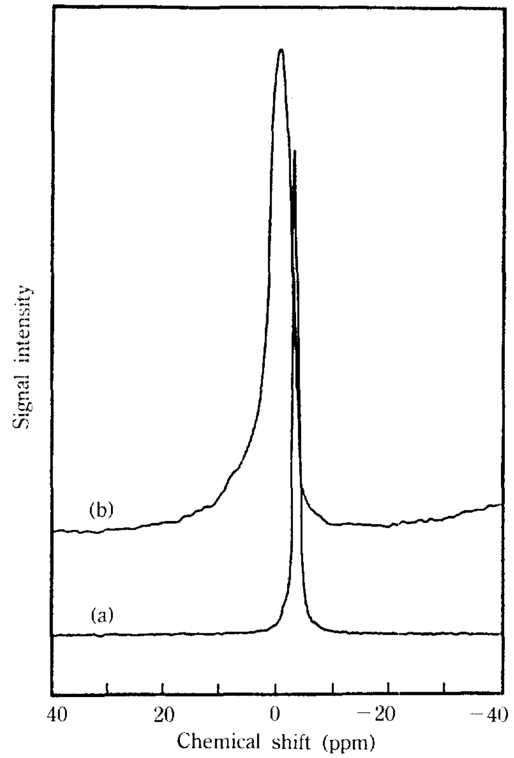

Fig. 4. ^{11}B MAS NMR spectra of the fully hydrated [B]ZSM-5 (a) as synthesized and (b) calcined at 750℃.

rupole coupling constant (<0.5 MHz). However, trigonal BO_3 units had rather a broad band because the quadrupole coupling constant (2.6-2.9 MHz) was larger than that of the tetrahedral BO_4 units. Scholle and Veeman [3] reported that the dehydration of [B]ZSM-5 made the highly symmetric tetrahedral BO_4 units distorted to much lower symmetry, resulting in substantial quadrupole interaction. Thus, in order to avoid NMR line broadening due to partial dehydration, all the samples were fully hydrated in a desiccator containing aqueous NH_4Cl solution for 48 hours before obtaining ^{11}B NMR spectra. Fig. 4(a) and (b) showed ^{11}B NMR spectra of the fully hydrated [B]ZSM-5 as synthesized and calcined at 750℃, respectively. A symmetric and narrow band was observed at −3.9 ppm with a half-band width of 50 Hz for the [B]ZSM-5 as synthesized. This band confirmed that most of B atoms are incorporated into the tetrahedral sites of the ZSM-5 structure during crystallization [2-4].

However, for the [B]ZSM-5 calcined at 750℃, then fully hydrated at room temperature, the band observed at −1.4 ppm was broader and more asymmetric than that of the [B]ZSM-5 as synthesized. The half-band width of [B]ZSM-5 calcined at 750℃ was about 5 times as large as that of [B]ZSM-5 as synthesized. If B atoms still remain in the tetrahedral sites of the ZSM-5 structure after calcination at 750℃, the half-band width and the chemical shift must be nearly the same as that of [B]ZSM-5 as synthesized because [B]ZSM-5 calcined at 750℃ was fully hydrated before obtaining a NMR spectrum [3, 4]. It was recently reported that the transformation between tetrahedral BO_4 and trigonal BO_3 units is reversible upon dehydration and rehydration [3, 4]. Therefore, the NMR line broadening and the irreversible transformation in the ^{11}B NMR band of [B]ZSM-5 calcined at 750℃ are due to the irreversible conversion from the highly symmetric tetrahedral BO_4 units to the lower symmetric BO_3 units during calcination.

The binding energies of [B]ZSM-5 as synthesized, calcined at 600℃, and calcined at 750℃ are given in Table 1, respectively. The correction factor for charging was smaller for [B]ZSM-5 calcined at 750℃ than for [B]ZSM-5 as synthesized and calcined at 600℃. The binding energies corresponding to [B]ZSM-5 as synthesized and [B]ZSM-5 calcined at 600℃ were nearly same. B(1s) binding energies for [B]ZSM-5 as synthesized and calcined at 600℃ were 197.5 and 198.0 eV, respectively. For the [B]ZSM-5 calcined at 750℃, however, B(1s) binding energy was 193.8 eV and lower than that of [B]ZSM-5s as synthesized and calcined at 600℃. Most boron compounds having +3 oxidation states containing trigonal BO_3 unit have B(1s) binding energies between 192 and 193 eV [15]. Another important observation was that the intensity of B(1s) binding energy band for [B]ZSM-5 calcined at 750℃ was approximately 1.8 times higher than that

Table 1. Binding energies of [B]ZSM-5 after various pretreatments

Pretreatment condition	Binding energy (eV)						Correction factor (eV)
	C(1s)*	Si(2s)	Si(2p)	O(1s)	Al(2p)	B(1s)	
As synthesized	284.3	154.3	104.0	532.7	73.2	197.5	4.2
Calcined at 600℃	284.3	154.3	103.5	531.9	72.2	198.0	4.2
Calcined at 750℃	284.3	155.8	104.5	533.4	−	193.9	3.7

*The C(1s) (284.3 eV) from the zeolite was used as an internal standard.

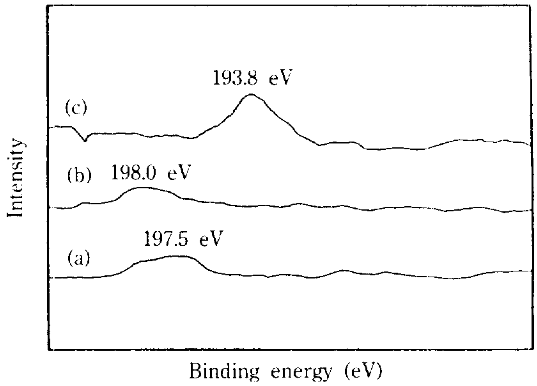

Fig. 5. XPS spectra of [B]ZSM-5 (a) as synthesized, (b) calcined at 600℃, and (c) calcined at 750℃.

of [B]ZSM-5 as synthesized or calcined at 600℃(Fig. 5). Therefore, it is concluded that considerable differences in the B(1s) binding energy values and band intensities between [B]ZSM-5 as synthesized and calcined at 750℃ is due to the release of tetrahedral BO_4 units from the ZSM-5 structure and the migration to the exterior surface as trigonal BO_3 units during calcination at 750℃. Surface enrichment of boron compound was clearly evidenced by the increase of the intensity of B(1s) band after calcination at 750℃, because XPS technique is sensitive to detect elements present in the vicinity of the surface of the sample.

CONCLUSION

1. IR, XRD, and ^{11}B MAS NMR results indicated that [B]ZSM-5 ($SiO_2/Na_2O=63.9$) and amorphous borosilicate ($SiO_2/Na_2O=50.9$) were converted to α-cristobalite and that B atoms in the ZSM-5 structure were converted to crystalline B_2O_3 phase having cubic symmetry after calcination at 750℃.

2. ^{11}B MAS NMR and XPS results indicated that calcination at 750℃ caused B atoms to be released from the tetrahedral sites of the ZSM-5 structure and migrated to the exterior surface of zeolite as a boron compound having trigonal BO_3 units and a oxidation state of 3.

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