

Nitride formation by the carbothermal reduction of a zeolite-polyacrylonitrile inclusion compound

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An inclusion compound between zeolite and polyacrylonitrile has been applied as a precursor for the carbothermal reduction process. By heat treatment at 1400 to 1600°C in N₂, β-sialon was mainly obtained. The X phase, α-Si₃N₄, the 15R-AlN phase, AlN, and mullite also formed under certain firing conditions. On the other hand, α-Si₃N₄ was detected as the principal crystalline phases as well as β-sialon in the products from zeolite-carbon mixtures. Hence, the use of the inclusion compound was advantageous for β-sialon production in the conversion of zeolite to nitrides.

1. Introduction

β-sialon (Si_{6-2z}Al_{2z}O_{2z}N_{8-2z}, z ≐ 0 to 4.2) [1] can be prepared directly from compounds having SiO₂-Al₂O₃ compositions by carbothermal reduction, although it is usually obtained by the hot-pressing of Si₃N₄ with other phases (Si₃N₄-SiO₂-AlN or Si₃N₄-Al₂O₃-AlN) [2]. Since a large amount of silicon exists as aluminosilicates, the preparation from naturally occurring aluminosilicates has been investigated recently; successful conversion from kaolinite [3-9], volcanic ash [10], montmorillonite [11, 12], pyrophyllite [6], and illite [8] has been reported.

In the carbothermal reduction processes, intimate mixing seems to be favourable for the reaction. Hence, the present authors applied a host-guest compound having two-dimensional ordering (a so-called "intercalation compound") as a precursor for β-sialon production, since it can be regarded as an extremely intimate mixture of oxides and carbonaceous materials [10, 11]. As a host material, montmorillonite, which was a swelling layered aluminosilicate, was utilized, and its intercalation compound with polyacrylonitrile (PAN) was converted to nitrides. A comparison with the reactions of montmorillonite-carbon mixtures revealed that suppression of the crystallization of the oxides was characteristic of the intercalation compound.

On the other hand, some materials having a three-dimensional structure also take up other species to form "inclusion compounds". Zeolites are typical host aluminosilicate minerals. Its rigid framework consists of (Si, Al)O₄ tetrahedra to form cavities. Cations and water molecules (so-called "zeolitic water") are present in the cavities. The cations in the cavities are exchangeable. Also, other neutral species can be adsorbed instead of the zeolitic water. However, the guest molecules are completely restricted on the

basis of their volume. Thus, the zeolites are known as "molecular sieves" [13].

In the present study, a zeolite-PAN inclusion compound was prepared and applied as a precursor for β-sialon production by carbothermal reduction. The process with the zeolite-PAN inclusion compound was characterized by comparing it with that of zeolite-carbon mixtures. Through this study, information on the effect of the mixing conditions on the nitridation of the aluminosilicates by carbothermal reduction will be obtained.

2. Experimental procedure

2.1. Preparation of zeolite-PAN inclusion compound

As zeolite, a hydrogen form (HY) of Y zeolite (SH-Y from Toyo Soda Manufacturing Co., Ltd, Tokyo) was utilized to prevent the influence of metal cations in the cavities on the reactions. Its composition on dry basis was as follows (in wt %): SiO₂ 77.3, Al₂O₃ 21.8, Na₂O 0.14 (total 99.2%). Its iron content was below the value corresponding to 0.1 wt % of Fe₂O₃. Its X-ray diffraction (XRD) pattern (using a Rigaku Denki RAD-IIA with manganese-filtered FeKα) showed the presence of no crystalline impurities.

Zeolite was initially heated at 200°C for 2 h in N₂ for dehydration, since water molecules and neutral guest molecules can occupy the same adsorption sites [13]. It was then soaked in an excess of acrylonitrile monomer containing 0.7 wt % of benzoyl peroxide as an initiator for 24 h at ambient temperature for its adsorption. After supernatant monomer was removed, the product was heated at 50°C for 24 h to polymerize the monomer. The crude product was then heated in air at 220°C for 48 h to cyclize PAN.

The amount of PAN in the product after heat treatment at 220°C was determined by the use of

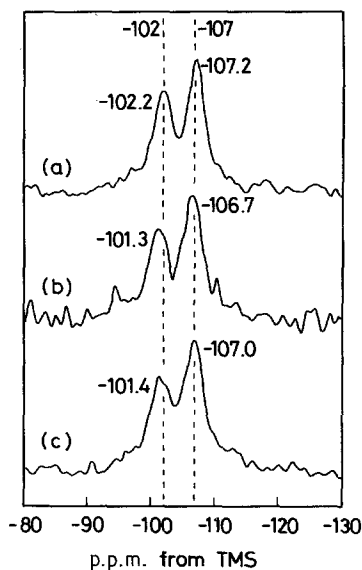


Figure 1 ^{29}Si MASNMR of the products: (a) raw zeolite, (b) zeolite-PAN inclusion compound, (c) heat-treated zeolite-PAN inclusion compound.

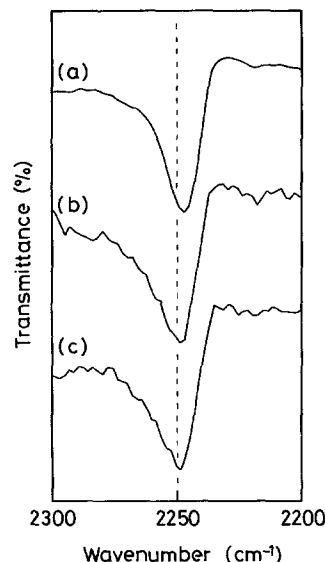
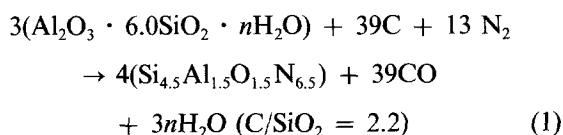


Figure 2 IR spectra of the products in the $\text{C}\equiv\text{N}$ stretching region: (a) zeolite-PAN inclusion compound, (b) zeolite-PAN inclusion compound treated with DMF for 1 h, (c) zeolite-PAN inclusion compound treated with DMF for 48 h.

thermogravimetry (TG) (Shimadzu TGA-20) to be 46 wt %. Since the reported yield of carbon fibre from PAN was about 50% [14], half of the heat-treated PAN was assumed to transform to carbon. When the amount of carbon was expressed as a molar ratio of carbon to the SiO_2 component of zeolite (C/SiO_2), the ratio was calculated to be ca. 3.5.

2.2. Preparation of zeolite-carbon mixtures

To obtain the zeolite-carbon mixtures, zeolite and carbon black (Koso Chemical Co., Ltd, Tokyo, $< 22 \mu\text{m}$) were mixed with an excess of n-hexane. The mixing ratio varied from $\text{C}/\text{SiO}_2 = 1$ to 5. For the variation in reaction temperature, the theoretical ratio due to the following ideal equation for the complete conversion to β -sialon was utilized:



After n-hexane was evaporated, the mixtures were crushed to pass a 100-mesh sieve.

2.3. Heat treatment

Both kinds of sample were placed in an Al_2O_3 boat ($\leq 1400^\circ\text{C}$) or a BN boat ($\geq 1500^\circ\text{C}$) and heated under an N_2 flow for 2 h. The reaction temperature varied from 1200 to 1600°C. The heating and cooling rates were 5°C min^{-1} in all the experiments.

2.4. Analyses

The zeolite-PAN inclusion compound was analysed by using high-resolution ^{29}Si nuclear magnetic resonance spectroscopy with magic-angle spinning (MASNMR) (Jeol GSX270 with frequency 53.67 MHz, pulse repetition time 5 sec, scans 256 to 446) to confirm

the presence of PAN in the cavities. In addition, the removal of PAN adsorbed on the external surface of zeolite was attempted by extraction with dimethylformamide (DMF). About 30 mg of the compound was stirred in ca. 30 ml of DMF for various hours. After centrifugation, the resulting products were again washed with the same amount of DMF. They were subsequently centrifuged and dried. The products were analysed by using infrared (IR) spectroscopy (JASCO FT/IR-5M, KBr method, resolution 2 cm^{-1} in the analysis of the inclusion compound and 4 cm^{-1} in that of the fired products) and differential thermal analysis (DTA) (Shimadzu DT-20B). The cyclized product was also characterized by using ^{29}Si MASNMR and IR spectroscopy (Shimadzu IR-435, KBr method).

Fired products were analysed by using XRD to identify crystalline phases. To express the behaviour of the phases, the peak intensities were quantitatively measured. The Miller indices and the d values of the peaks used (in nm) are as follows: β -sialon (110), $d = 0.380^*$; α - Si_3N_4 (101), $d = 0.432$; the O' phase [1] (020), $d = 0.444^*$; the X phase (210), $d = 0.559$; the 15R-AlN phase [1] (00 $\bar{2}$), $d = 0.199$; AlN (110), $d = 0.156$; AlON ($\text{Al}_{8/3+x/3}\text{O}_{4-x}\text{N}_x$) (311), $d = 0.239$; mullite (110), $d = 0.539$; cristobalite (101), $d = 0.405$. The reported I/I_0 ratio for the (110) line of β - Si_3N_4 is 35, and the observed value for β -sialon was similar (ca. 50). On the other hand, the (101) line of α - Si_3N_4 was the strongest peak in the present systems, though its reported ratio is 50. Approximate z values of β -sialon were determined from the positions of its (200) peaks. Also, IR spectra (Jasco FT/IR-5M as above) of the products were recorded to obtain information on the amorphous phases. The morphology of the products was studied by a scanning electron microscope (SEM) (Hitachi S-570).

*The d values are for β - Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$, respectively.

3. Results and discussion

3.1. Thermal transformation of zeolite

By XRD analysis of the raw zeolite heated at 1100 to 1400°C in N₂ for 2 h, mullite and cristobalite were detected as crystalline phases. Mullite formed in all the heating conditions; a poorly crystallized type was still obtained even after the treatment at 1400°C. Cristobalite crystallized only by the treatment at 1400°C. Therefore, a large amount of the SiO₂ component was present as an amorphous form after treatments below 1300°C.

3.2. Synthesis of the zeolite-PAN inclusion compound

The inclusion of acrylonitrile (AN) and its subsequent polymerization in the cavities of HY zeolite as well as on the external surface were initially investigated. On the basis of the pore size (~0.7 nm), the incorporation of AN was probable. However, no evidence was obtained by using XRD, since no structural changes occurred because of the rigid three-dimensional structure. A zeolite-AN inclusion compound was reported by Petfield *et al.* [15] for CsX zeolite which was classified in the faujasite group, as well as Y zeolite. They demonstrated its inclusion by spectroscopic evidence, and further reported its polymerization in the cavities. In the present study, the inclusion of PAN was studied by using ²⁹Si MASNMR and IR spectroscopy.

Fig. 1 shows the ²⁹Si MASNMR spectra of the products. The NMR spectra suggest the presence of PAN in the cavities. The raw zeolite demonstrated two signals at -102.2 and -107.2 p.p.m. (Fig. 1a). The former was ascribed to the silicon atom which was surrounded by one aluminium via oxygen bridges among four positions (abbreviated as Si(1Al)) [16]. The other one was assigned to Si(0Al), using the same abbreviation. After the treatment with AN and its subsequent polymerization, both the signals slightly shifted to lower field in comparison with those of the raw zeolite (Fig. 1b). In terms of intercalation compounds, which form another group of guest-host complexes having molecular-level intimacy, the incorporation of the guest molecules in the interlayer space and the resulting expansion slightly affect the chemical shifts of the ²⁹Si signals [17]. Therefore, one can assume that the present observation may also be ascribed to a change in the environment of silicon by the formation of the zeolite-PAN inclusion compound.

Fig. 2 shows the IR spectra of the products in the C≡N stretching region. The variation in the frequency of the C≡N stretching band of PAN with its extraction supports inclusion-compound formation. In the spectrum of the unextracted compound, the C≡N stretching band was observed at 2247 cm⁻¹ (Fig. 2a). By stirring in DMF for 1 h, the intensity of the exothermic peak at ca. 300°C on the DTA curve and that of the C≡N stretching band in the spectrum drastically decreased; a large amount of PAN was removed. After the treatment, the frequency shifted to 2249 cm⁻¹ (Fig. 2b). Even after the extraction for 48 h, the band was still detected at the same frequency (Fig. 2c). It is likely that PAN in the cavities is more resistant to its removal from the zeolite particles than

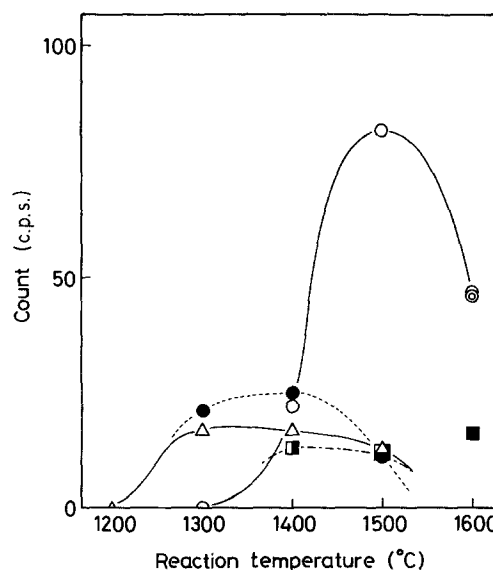


Figure 3 The variation in the composition with reaction temperature for zeolite-PAN inclusion compound (heating time 2 h). (O) β -sialon, (●) α -Si₃N₄, (■) X phase, (■) 15R-AlN, (⊙) AlN, (Δ) mullite.

that adsorbed on the external surface of zeolite. Hence, the shifted frequency can be ascribed to PAN in the cavities. The slight shift may be attributed to the interaction with hydrogen of the hydroxyl of zeolite, or that of the water molecules in the cavities.

By heat treatment at 220°C for 48 h, PAN seemed to be cyclized even in the cavities. The IR spectrum of the heat-treated product demonstrated that the intensity of the C≡N stretching band drastically decreased. Correspondingly, a new band appeared at ca. 1580 cm⁻¹, which was assigned to a C=C or a C=N stretching mode [18]. The ²⁹Si MASNMR spectrum of the heat-treated product (Fig. 1c) showed a slightly different profile from that of the raw zeolite. Therefore, polymeric species must still be present in the cavities.

3.3. Reactions of the zeolite-PAN inclusion compound

Fig. 3 shows the variation in the composition of the products with reaction temperature. Mainly β -sialon was formed by heating the inclusion compound, especially at 1500°C. At 1300°C, reduction and nitridation occurred, so that traces of α -Si₃N₄ and β -sialon were obtained. In the reactions at 1400°C, nitride formation was accelerated; β -sialon and the X phase formed, with the presence of a trace of α -Si₃N₄. When the inclusion compound was heated at 1500°C, small amounts of α -Si₃N₄ and the X phase were detected as well as β -sialon.

On heating at 1600°C, the composition of the product greatly differed from the others. As the main crystalline phases, β -sialon, the 15R-AlN phase and AlN were detected. In comparison with the reactions at 1500°C, a smaller amount of β -sialon was obtained. AlN formed only by the treatment at 1600°C. Although α -Si₃N₄ formation was observed by the treatments below 1500°C, it was not detected in the product heated at 1600°C. Since α -Si₃N₄ was less stable than β -Si₃N₄ at higher temperature, this

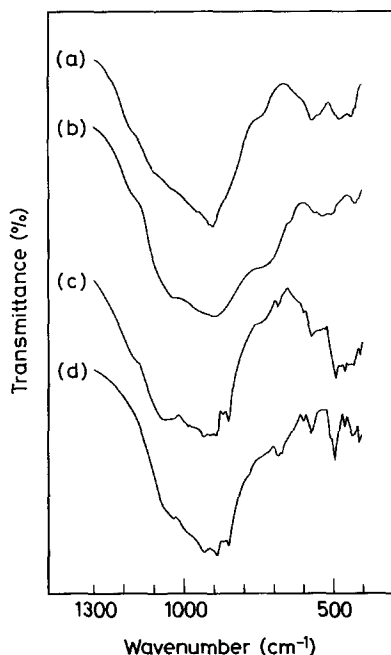


Figure 4 IR spectra of the products. From inclusion compound: (a) heated at 1400°C for 2 h and (b) at 1500°C for 2 h. From mixture ($C/SiO_2 = 2.2$): (c) heated at 1400°C for 2 h and (d) at 1500°C for 2 h.

observation was ascribed to the suppression of its initial formation and/or its conversion to β -sialon via its transformation.

As oxides, only mullite was obtained by the treatment at 1200 to 1500°C, although both mullite and cristobalite formed by heating the raw zeolite at 1400°C for 2 h. The variation in the peak intensity of mullite showed that it was not remarkably reduced even by the treatment at 1500°C for 2 h. However, it was completely reduced by the treatment at 1600°C within 2 h.

Fig. 4 shows the IR spectra of the products. The product heated at 1400°C for 2 h (Fig. 4a) showed a strong band at 898 cm^{-1} which was assigned to an Si-N stretching mode [19, 20]. The band had a clear shoulder at around 1100 cm^{-1} . Since mullite showed no strong bands at around 1100 cm^{-1} [21], the shoulder was ascribed to an Si-O stretching band of an amorphous phase. By the treatment at 1500°C, the band at ca. 1100 cm^{-1} disappeared, which indicated the reduction of most of the amorphous phase (Fig. 4b).

The approximate z values of β -sialon were found to be 3.7 and 3.1 for the products heated at 1500°C for 2 h and at 1600°C for 2 h, respectively. If the original composition is assumed to be maintained during the conversion, the z value becomes 1.5 (see Equation 1). Hence, the obtained β -sialon contained a larger amount of aluminium.

Fig. 5 shows the morphology of the products. When the zeolite-PAN inclusion compound was heated at 1400°C for 2 h (Fig. 5a), the formation of fine products on the surface of the particles was observed. Some of the particles were mainly covered with the whiskers (Fig. 5b).

3.4. Reactions of the zeolite-carbon mixtures

Fig. 6 demonstrates the variation in the composition

with the C/SiO_2 ratio, when the mixtures were heated at 1400°C for 2 h. With all the C/SiO_2 ratios, the amounts of α - Si_3N_4 were larger than those of β -sialon. α - Si_3N_4 was detected in all the products. On the other hand, β -sialon was obtained when the C/SiO_2 ratio was above 2. In addition, the sialons of the O' phase and the X phase were detected. As oxides, mullite and cristobalite formed. Mullite was obtained from all the mixtures.

The effect of reaction temperature is shown in Fig. 7. In the reactions at 1400 and 1500°C, α - Si_3N_4 formation was predominant. When the mixture was heated at 1400°C, reduction and nitridation occurred. As principal phases, α - Si_3N_4 and the X phase were obtained. On the other hand, only a trace of β -sialon was detected. By the treatment at 1500°C, nitridation proceeded to a great extent. α - Si_3N_4 and β -sialon were mainly detected in the product. In addition, the X phase and aluminium oxynitride (AlON) were obtained.

In the reactions at 1600°C, the amount of β -sialon increased, while a smaller amount of α - Si_3N_4 formed. This was ascribed to the instability of α - Si_3N_4 at higher temperature, which was also observed in the reactions of the inclusion compound. By the treatment at 1600°C, no amounts of the X phase were obtained. From the Al_2O_3 component, AlN formed as well as AlON.

Mullite was present in the products heated below 1500°C, while cristobalite formed by the treatments at 1300 and 1400°C. No amounts of oxides were detected after the treatment at 1600°C.

The IR spectra of the products are shown in Fig. 4. The spectrum of the product heated at 1400°C (Fig. 4c) revealed the presence of the characteristic bands due to α - Si_3N_4 and β -sialon [20, 22]. Also, a broad band due to the Si-O stretching mode was observed at 1068 cm^{-1} , which indicated the presence of the amorphous phase in the product. By the treatment above 1500°C the band at ca. 1100 cm^{-1} disappeared (Fig. 4d). This observation suggests the reduction of most of the amorphous phase.

The compositions of β -sialon were also determined in the same manner as applied to those of the inclusion compound. The z values of β -sialon were found to be ca. 2 to 3, which were slightly smaller than those of the inclusion compound.

The characteristic shape of the product (from the mixture with $C/SiO_2 = 2.2$ heated at 1400°C) is shown in Fig. 5c. In the reactions of the mixtures, the particles were usually covered with whiskers.

3.5. Reaction mechanisms

The reactions proceeded heterogeneously in both the systems. From the SiO_2 and the Al_2O_3 components, sialons, especially β -sialon, were obtained. The SiO_2 component was also converted to α - Si_3N_4 . From the Al_2O_3 component, AlN and/or AlON formed by the treatment at higher temperature. As oxides, mullite was mainly crystallized.

The obvious difference arisen from the mixing condition was observed in the α - Si_3N_4 / β -sialon ratio in the products. The intimate mixing in the zeolite-PAN

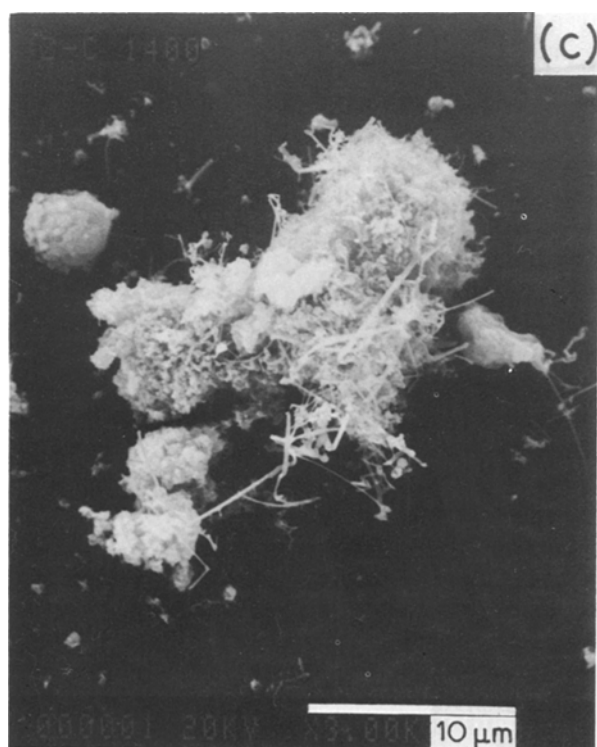
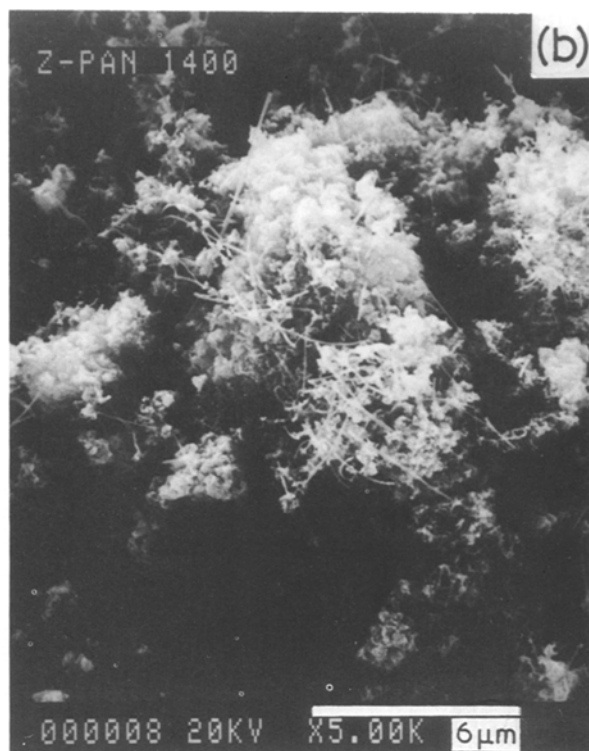
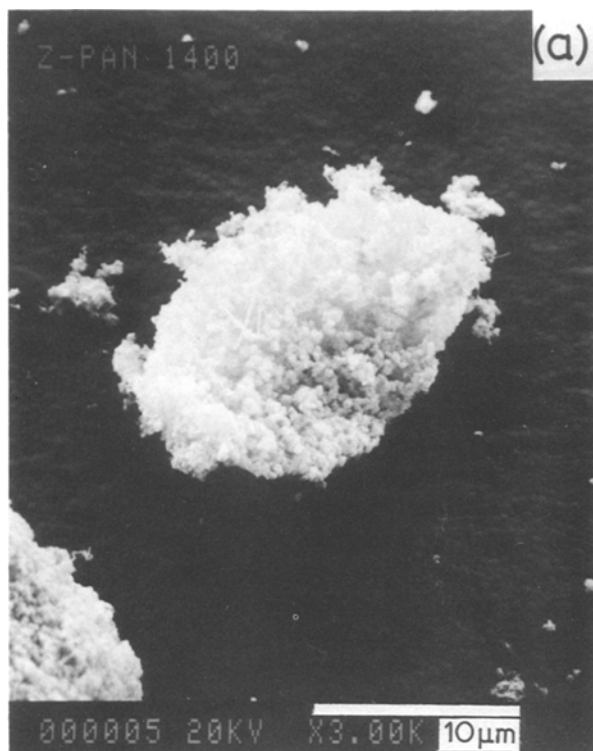


Figure 5 Scanning electron micrographs of the products: (a, b) zeolite-PAN inclusion compound heated at 1400°C for 2h; (c) zeolite-carbon mixture ($C/SiO_2 = 2.2$) heated at 1400°C for 2h.

completely ascribed to the mixing conditions, because they may be due to their different carbon contents.

From the XRD patterns of the products, SiC formation was hard to confirm because of the overlapping of the strongest peak of β -SiC with those of β -sialon and/or the 15R-AlN phase ($d = 0.252$ nm). However, its possible amounts were small, since no other peaks due to SiC were observed.

The zeolite-PAN inclusion compound and the zeolite-carbon mixtures showed similar reactivities, although the montmorillonite-PAN intercalation compound demonstrated higher reactivities than the montmorillonite-carbon mixtures. Montmorillonite shows a two-dimensional structure and the resulting

inclusion compound was favourable for β -sialon formation. This was not ascribed to the different carbon contents, since α -Si₃N₄-rich compositions were obtained from all the mixtures having various carbon contents.

Moreover, additional differences in the crystalline compositions were observed; the 15R-AlN phase formed only from the inclusion compound, whereas AlON and cristobalite were obtained only from the mixtures. Also, traces of β -sialon and α -Si₃N₄ were formed by the treatment at 1300°C only from the inclusion compound. These observations cannot be

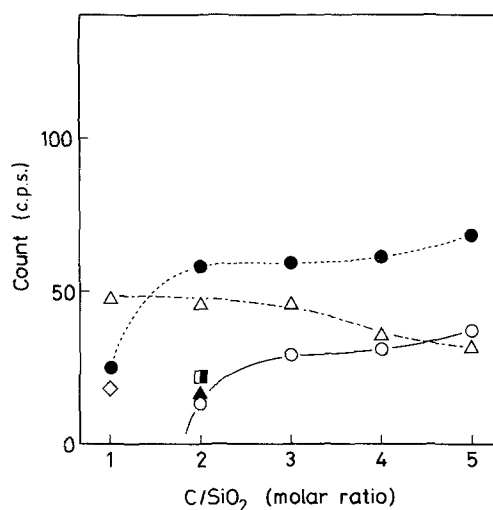


Figure 6 The variation in the composition with the C/SiO_2 ratio for zeolite-carbon mixtures (reaction temperature 1400°C, heating time 2 h). (○) β -sialon, (●) α -Si₃N₄, (◇) O' phase, (■) X phase, (△) mullite, (▲) cristobalite.

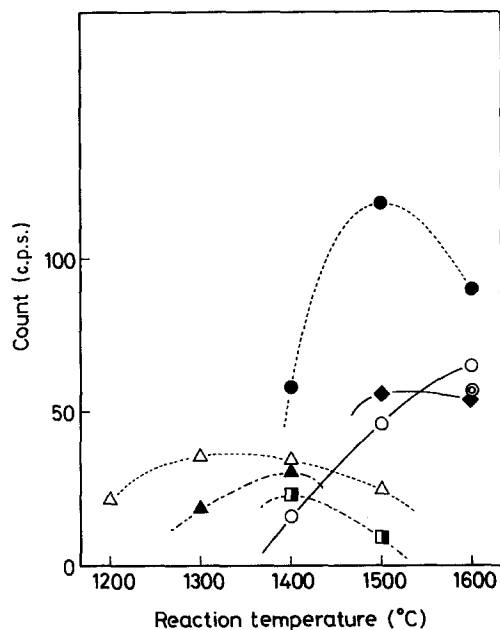


Figure 7 The variation in the composition with reaction temperature for zeolite-carbon mixtures ($C/SiO_2 = 2.2$, heating time 2 h). (○) β -sialon, (●) α -Si₃N₄, (■) X phase, (⊙) AlN, (◆) AlON, (▲) mullite, (▲) cristobalite.

swelling property. Therefore, a large amount of PAN can be incorporated in the interlayer space in a layered conformation. Such conditions seemed to be preferable for its graphitization. In addition, the presence of the PAN layer in the interlayer space led to the suppression of the crystallization of the oxides, since the PAN layer completely separated the individual silicate layer.

On the other hand, the zeolite has a rigid three-dimensional structure, so that only a limited amount of PAN can be present in the restricted space of the cavities. Hence, a smaller amount of PAN can contribute to intimate mixing with the oxides in the zeolite-PAN inclusion compound in comparison with that in the montmorillonite-PAN intercalation compound. Also, PAN cannot prevent the crystallization of mullite because of the rigid network of the oxides. Thus, a remarkable increase in the reactivity due to inclusion compound formation was not observed.

4. Conclusions

The zeolite-PAN inclusion compound was heated in N₂ at 1200 to 1600°C for converting zeolite to nitrides by carbothermal reduction. For comparison, the zeolite-carbon mixtures were also heated similarly. From both of them, α -Si₃N₄, β -sialon, AlN, and the X phase formed as principal crystalline nitrides. As oxides, mullite was mainly obtained. The mixing condition influenced the compositions of the products, especially the α -Si₃N₄/ β -sialon ratio. The intimate

mixing in the inclusion compound was favourable for obtaining β -sialon-rich powder. Thus, the zeolite-PAN inclusion compound has a potential as a precursor for β -sialon production.

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