

Thermal decomposition of mechanically activated gibbsite

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Abstract

Gibbsite ($\text{Al}(\text{OH})_3$) was mechanically activated by grinding for 20 h, and the changes in its structure were studied by thermal analysis, X-ray powder diffraction and ^{27}Al MAS NMR. Grinding caused the rupture of a significant proportion of the Al–OH bonds, but the resulting molecular water was immediately adsorbed on to the activated surfaces from which it could be endothermically desorbed at 125°C. Grinding causes the gibbsite to become X-ray amorphous, containing octahedral and tetrahedral sites, and another site at about 34 ppm sometimes ascribed to Al in 5-fold coordination; the relative site occupancies suggest that this phase is similar to $\rho\text{-Al}_2\text{O}_3$. The amorphous phase converts via $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ (corundum) at 900°C, by contrast with unactivated gibbsite which transforms to corundum via γ and $\theta\text{-Al}_2\text{O}_3$ at least 400°C higher. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Gibbsite, $\text{Al}(\text{OH})_3$, has a crystal structure in which the Al is octahedrally coordinated with double layers of hexagonal close-packed hydroxyl groups stacked in an AB BA sequence [1]. When heated in air, the hydroxyls are eliminated as water at about 320°C [2], transforming to α -alumina (corundum) via a sequence of hexagonal close packed transition aluminas (χ and κ -alumina [3]). An alternative thermal reaction sequence involves the initial formation of boehmite and its transformation via the cubic spinel transition phases γ , δ and θ -alumina [3]. All the transition aluminas contain both tetrahedral and octahedral Al, the proportion of tetrahedral sites increasing

slightly with increasing formation temperature, from χ (typically 29% tetrahedral) to γ (typically 32% tetrahedral [4]). The cubic transition phases have spinel-like structures in which protons have been suggested to play a stabilizing role [5]. The final product of thermal reaction, corundum, has a hexagonal structure in which all the Al atoms are again octahedrally coordinated.

When mechanically activated by vigorous grinding, many crystalline materials, including gibbsite, are known to lose their long-range order and become X-ray amorphous. The effect of grinding on the alumina hydrates, including gibbsite, was studied by Arai et al. [6] and Tsuchida and Ichikawa [7], who reported that grinding converts gibbsite into an X-ray amorphous phase which retains its water content and becomes ‘gel-like’ [6,7]. Thermal dehydration of this amorphous phase broadens the characteristic gibbsite dehydroxylation endotherm and lowers its tempera-

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ture to about 150–200°C [7]. The dehydrated product is also X-ray amorphous [7] and is thermally converted to α -alumina either via η -alumina [7] or via the γ - δ - θ sequence [6]. Smaller sample weights were more efficiently ground and were found to thermally transform via χ and κ -alumina [6]. The transformation temperature of the ground gibbsite to α -alumina is lowered by >200°C [6,7]. Thermal conversion of gibbsite under reduced pressure (10^{-2} Torr) to α -alumina occurs directly, without the formation of crystalline intermediates [6].

The nature of the Al–O bonding in the X-ray amorphous phase is presently unknown, and the change in the Al environment during thermal reaction, which is expected to be significantly modified by mechanochemical activation, has not previously been studied.

Solid state nuclear magnetic resonance spectroscopy with magic angle spinning (MAS NMR) has proved to be an excellent technique for investigating the changes occurring in amorphous materials in the regions of their thermal reaction sequences which are not accessible to X-ray diffraction (XRD). The present study utilises ^{27}Al MAS NMR, in conjunction with thermal analysis and XRD, to investigate the constitution and thermal reactions of gibbsite which has been mechanochemically amorphized, and to compare its thermal behaviour with that of unactivated gibbsite.

2. Experimental

The gibbsite was Grade H-43 M (Showa Denko Co. Ltd., purity 99.6%, BET specific surface area $8\text{ m}^2\text{ g}^{-1}$). XRD showed it to be crystalline monophase gibbsite. Amorphization was carried out by grinding for 20 h in a planetary pot mill (La-PO.1, ITOH, Japan) at a rotation speed of 400 rpm using a silicon nitride pot and milling media. Thermal analysis of the ground and unground materials was carried out on 10 mg samples at a heating rate of $10^\circ\text{C min}^{-1}$ in flowing air (50 ml min^{-1}) using a Rheometrics STA 1500 thermoanalyser. Portions of the ground and unground gibbsite were heated isothermally for 15 min in platinum crucibles in an electric muffle furnace, at temperatures chosen with reference to the thermal analysis curves. After heating, the samples were examined by XRD (Philips PW1700 computer-

controlled diffractometer with a graphite monochromator and $\text{CoK}\alpha$ radiation). ^{27}Al MAS NMR was carried out at 11.7 T using a Varian Unity 500 spectrometer with a 5 mm Doty MAS probe spun at 12 kHz. A 15° pulse of $1\ \mu\text{s}$ was used, with a recycle delay of 1 s, and the spectra were referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

3. Results and discussion

The thermal analysis curves for ground and unground gibbsite are shown in Fig. 1(A) and (B), respectively.

The present unground gibbsite dehydrates in a single endothermic step at 295°C corresponding to a mass loss of 27.9% at 300°C . A further gradual mass loss of 5.4% is complete by 700°C (Fig. 1(B)); the total loss of 33.3% is in reasonable agreement with the

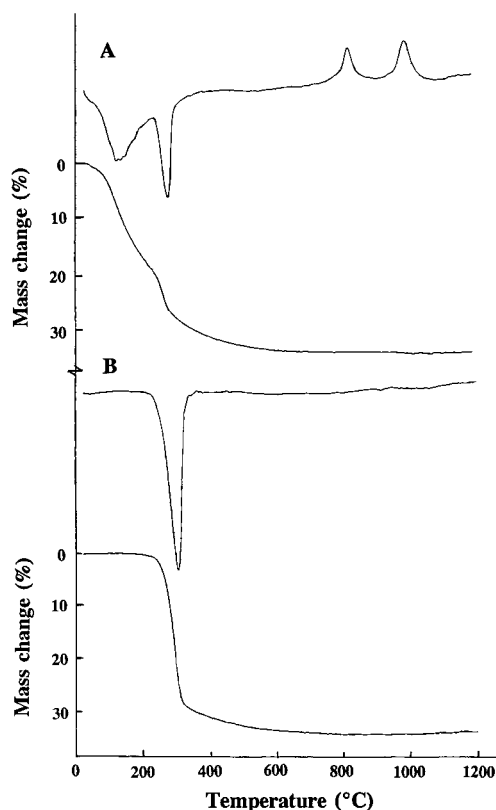


Fig. 1. TG and DSC curves of (A) gibbsite ground for 20 h, (B) unground gibbsite. Heating rate $10^\circ\text{C min}^{-1}$ in flowing air (50 ml min^{-1}).

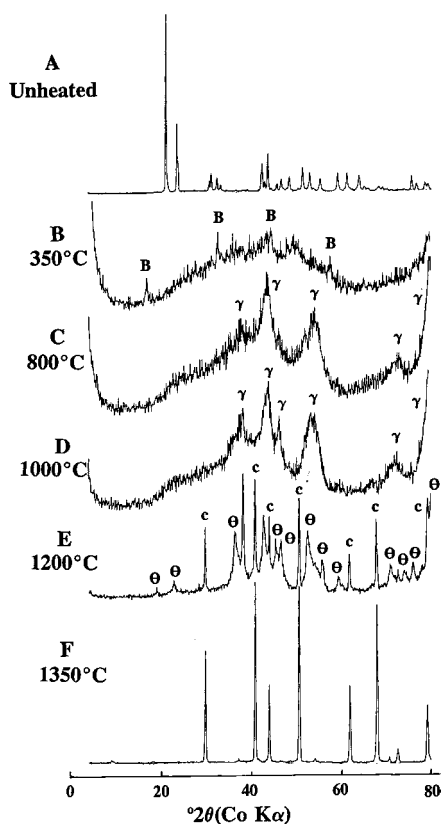
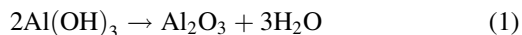


Fig. 2. Powder X-ray diffractograms of unground gibbsite, heated for 15 min at the indicated temperatures. Key: B = boehmite (PDF no. 21-1307), $\gamma = \gamma\text{-Al}_2\text{O}_3$ (PDF no. 10-425), c = corundum (PDF no. 10-173), $\theta = \theta\text{-Al}_2\text{O}_3$ (PDF no. 11-517). Unmarked peaks in trace (A) correspond to gibbsite (PDF no. 33-18), those in trace (F) correspond to corundum.

theoretical value of 34.6% for the reaction:



No further thermal events occur in the present unground gibbsite up to 1200°C. Grinding this gibbsite for 20 h changes the shape of the dehydration endotherm (Fig. 1(A)), which is split into two consecutive events. The first broad endotherm occurs at $\approx 125^\circ\text{C}$ and represents a mass loss of $\approx 18.7\%$. The second, sharper endothermic peak occurring at 268°C is accompanied by a mass loss of 7.2%. A further gradual mass loss of 7.9% is complete at 620°C , the total loss at this temperature being 33.8%, again in agreement with Eq. (1). The two exothermic features

which occur at 820°C and 990°C have no associated mass change (Fig. 1(A)).

X-ray powder diffraction of the present unground gibbsite heated to various temperatures (Fig. 2)) shows that the product of heating to just above the dehydration endotherm (Fig. 2(B)) has lost all the original gibbsite reflections and is essentially amorphous, but with a few weak features arising from a small trace of boehmite, $\gamma\text{-AlOOH}$. Heating to 800°C , above the temperature of complete dehydration, results in the appearance of several broad, diffuse reflections corresponding to $\gamma\text{-Al}_2\text{O}_3$ (Fig. 2(C)). These $\gamma\text{-Al}_2\text{O}_3$ reflections continue to develop gradually with further heating to 1000°C (Fig. 2(D)), but remain broad and diffuse. By 1200°C , the major lines of $\alpha\text{-Al}_2\text{O}_3$ have appeared (Fig. 2(E)), together with the pattern of the hexagonal transition alumina $\theta\text{-Al}_2\text{O}_3$, which occurs as an intermediate between γ and $\alpha\text{-Al}_2\text{O}_3$. The transition of γ to $\theta\text{-Al}_2\text{O}_3$ does not require major structural rearrangement, since in both phases the oxygen sublattice is similarly cubic close-packed. The increased order of the $\theta\text{-Al}_2\text{O}_3$ structure is reported to occur by alignment and merging of the lamellae, by adjustment of stacking faults in the (111) direction, and by diffusion of surface Al to more ordered sites [8]. The transformation to $\alpha\text{-Al}_2\text{O}_3$ is gradual, but is complete by 1350°C (Fig. 2(F)).

XRD shows that in the gibbsite sample ground for 20 h, all but the two strongest gibbsite reflections have been destroyed by grinding, and the intensity of these strongest reflections has been greatly decreased (Fig. 3(B)). Additional lines corresponding to bayerite ($\alpha\text{-Al}(\text{OH})_3$) are detectable above the amorphous background corresponding to the amorphized gibbsite. Bayerite differs from gibbsite principally in its AB AB layer sequence; it thus appears that one of the effects of grinding is to disrupt the layer structure during amorphization. Heating to just above the first dehydration endotherm produces almost no change in the XRD pattern, but the low temperature at which this significant mass loss occurs suggests that it represents structural (hydroxyl) water which was detached from the gibbsite during grinding, then reabsorbed as hydration water on the freshly activated surfaces of the amorphous product. Heating to above the second endotherm removes the remaining gibbsite and bayerite reflections and produces a totally amorphous XRD

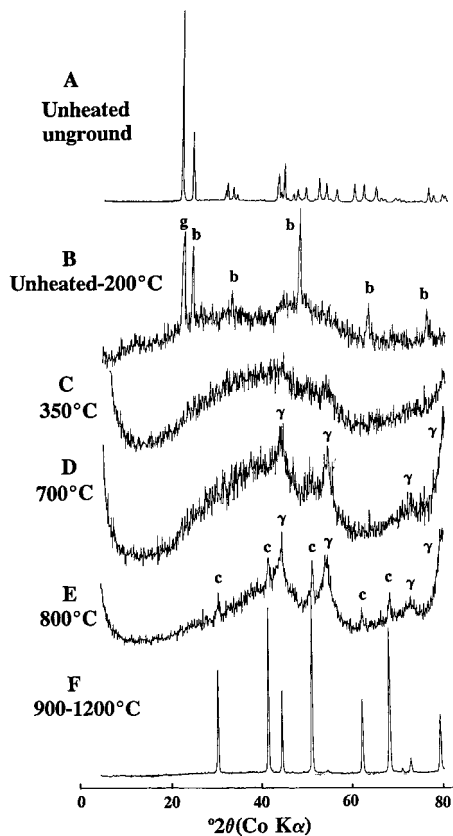


Fig. 3. Powder X-ray diffractograms (B–F) of gibbsite ground for 20 h, heated for 15 min at the indicated temperatures. Key: g = gibbsite (PDF no. 33-18), b = bayerite (PDF no. 15-136), γ = γ - Al_2O_3 (PDF no. 10-425), c = corundum (PDF no. 10-173). Unmarked peaks in trace (A) correspond to gibbsite, those in trace (F) to corundum.

pattern (Fig. 3(C)). The approximate correspondence of this endotherm temperature and that of unground gibbsite suggests that the small mass loss associated with this endotherm represents structural water from the regions of gibbsite not fully amorphized but which have acquired sufficient strain and/or defects to decrease the thermal stability by about 25°C. A similar decrease of thermal stability of the bayerite in the ground sample is suggested by the loss of these reflections by 350°C.

The XRD-amorphous phase gradually loses a further 7.9% water below the temperature of the first exotherm (820°C), with the appearance in this temperature range of the first diffuse XRD evidence of γ - Al_2O_3 (Fig. 3(D)). By 800°C, the γ - Al_2O_3 XRD reflec-

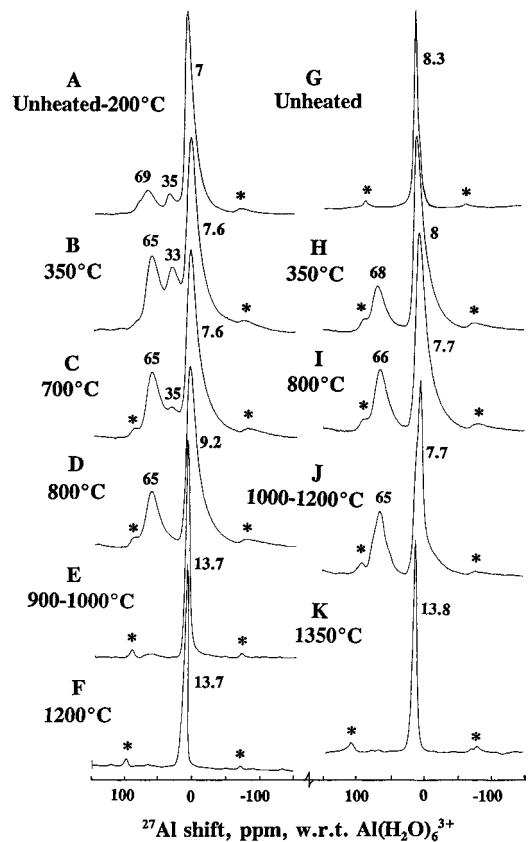


Fig. 4. 11.7T ^{27}Al MAS NMR spectra of gibbsite heated for 15 min at the indicated temperatures. (A–F), samples ground for 20 h, (G–K), unground gibbsite. Asterisks denote spinning side bands.

tions have sharpened and weak reflections of α - Al_2O_3 appear, superimposed on the broad XRD background of the amorphous material still present. By 900°C, complete transformation to well-crystallized α - Al_2O_3 has occurred. Since the thermal analysis experiment is conducted under dynamic heating conditions, the temperatures recorded for the thermal events are expected to lag behind those of the XRD samples, which were isothermally heated for 15 m at each temperature. Thus, the first exotherm (820°C) is likely to correspond to the formation of γ - Al_2O_3 from the amorphous phase, and the second exotherm (990°C) may be attributed to the abrupt transformation of γ to α - Al_2O_3 without the intervention of the usual intermediate aluminas such as δ and θ - Al_2O_3 .

3.1. ^{27}Al MAS NMR results

The ^{27}Al MAS NMR spectra of unground and ground gibbsite heated to various temperatures are shown in Fig. 4.

The unheated unground material (Fig. 4(G)) shows the single sharp octahedral resonance expected from the known structure of gibbsite and as reported by other authors [3]. Heating to just above the temperature of the endothermic water loss produces a new tetrahedral signal at 68 ppm (Fig. 4(H)). The appearance of tetrahedral Al is a consequence of the elimination of structural water with the formation of a close-packed oxygen lattice in which some of the tetrahedral interstices are occupied by Al. Although the long-range ordering of the dehydrated component in this sample is not sufficiently established to give an XRD pattern, the proportion of tetrahedral Al in this phase (estimated as 20.5% by curve-fitting the ^{27}Al NMR spectrum) is only slightly lower than reported at the same magnetic field strength for $\chi\text{-Al}_2\text{O}_3$ (27% [4]); the difference is probably due to the additional octahedral intensity arising from the trace of boehmite present. Heating to progressively higher temperatures produces a gradual increase in the proportion of Al in the tetrahedral sites, the tetrahedral occupancy at 1000°C being 28.9%, in reasonable agreement with the value of 30% reported for $\gamma\text{-Al}_2\text{O}_3$ at 11.7 T [4]. The transformation to $\alpha\text{-Al}_2\text{O}_3$, which is complete by 1350°C, is marked by the abrupt disappearance of tetrahedral Al and a change in the octahedral chemical shift from 7.7 ppm to a value typical of corundum (13.8 ppm). The changes in Al site occupancy on heating unground gibbsite are summarised in Fig. 5(A).

The ^{27}Al MAS NMR spectra of ground gibbsite (Fig. 4(A)) show that grinding has introduced two additional resonances, a tetrahedral peak at 65–69 ppm and a peak at 33–35 ppm which has been attributed to Al in 5-fold coordination with oxygen. Heating this sample to the temperature of the first endothermic water loss produces little change in the NMR spectrum, consistent with the suggestion that only hydration water is removed at this stage. After the second endothermic water loss, the NMR spectrum (Fig. 4(B)) shows an increase in both the tetrahedral and 34 ppm peaks at the expense of the octahedral resonance (Fig. 5(B)). This spectrum is similar to that

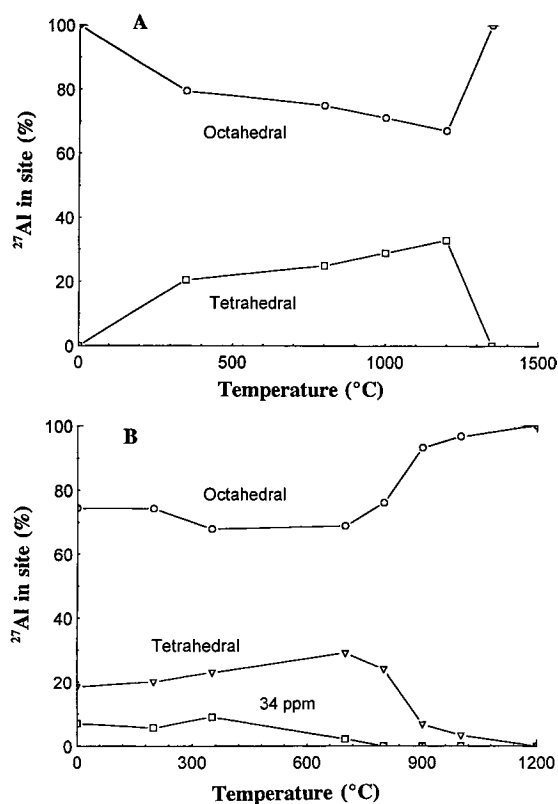


Fig. 5. Changes in ^{27}Al NMR site occupancy as a function of heating temperature. (A), unground gibbsite, (B), gibbsite ground for 20 h.

reported [4] for $\rho\text{-Al}_2\text{O}_3$, an ill-defined phase with an amorphous XRD pattern which is formed by dehydration of gibbsite at 100–400°C under reduced pressure [3]. The relative occupancy of the three distinguishable NMR sites in the present spectrum are in approximate agreement with those reported for a 14.1 T spectrum of $\rho\text{-Al}_2\text{O}_3$ spun at 15 kHz (55% octahedral, 20% 34 ppm, 25% tetrahedral [4]), but with less of the 34 ppm peak intensity. This apparent discrepancy in the peak area of the 33–35 ppm resonance may arise from the slower sample spinning speed (12 kHz) used in the present work; it has been reported [4] that this resonance is sensitive to spinning speed, the peak height increasing with faster spinning. Although ^{27}Al MAS NMR resonances at 30–35 ppm in $\rho\text{-Al}_2\text{O}_3$ and other X-ray amorphous Al-containing compounds including aluminosilicates and glasses are often ascribed to 5-coordinated Al, an alternative

explanation has been tentatively advanced, in terms of Al in an octahedral site adjacent to the oxygen vacancy in a defect spinel [4]. Although the nature of this particular site is still under discussion, the present results indicate that the amorphous product formed by grinding gibbsite contains Al in sites very similar to ρ - Al_2O_3 , in both its hydrated and dehydrated form.

Heating to higher temperatures $<800^\circ\text{C}$ brings about the progressive conversion of the 33–35 ppm site to tetrahedral sites (Fig. 5(B)) as poorly-ordered γ - Al_2O_3 is formed from the ρ - Al_2O_3 . Formation of α - Al_2O_3 $>800^\circ\text{C}$ is marked by the conversion of tetrahedral Al to octahedral; comparison of the XRD and NMR data suggests that the hexagonal oxygen lattice of corundum is established rather abruptly, with a subsequent gradual movement of Al into the octahedral sites.

The effect of grinding gibbsite may be summarised as follows:

1. Under the present grinding conditions, a significant proportion ($\approx 54\%$) of the Al–OH bonds are ruptured, leading to the formation of molecular water which is immediately reabsorbed on the freshly-activated surfaces. This mechanically-held water is desorbed on heating at 125°C , consistent with a previous report [7] that grinding is not accompanied by dehydration, but that the temperature of subsequent dehydration is lowered to 150 – 200°C .
2. The long-range atomic ordering in mechanically-altered gibbsite is destroyed, but the X-ray amorphous material contains, in addition to Al in tetrahedral and octahedral, Al sites which have a ^{27}Al MAS NMR resonance at about 34 ppm. The tetrahedral Al forms as a normal consequence of bimolecular elimination of water from adjacent hydroxyl groups. The 33–35 ppm site may arise either from Al in 5-fold coordination, or may represent 6-coordinate Al in the vicinity of an oxygen vacancy such as may occur in the defect spinel structures of the transition aluminas. Contributions to the octahedral Al NMR signal may come from residual unamorphized gibbsite as well as from the small quantity of bayerite also present which is apparently formed by disruption of the gibbsite layer sequence during grinding.

3. The subsequent thermal behaviour of both the residual gibbsite and bayerite indicates that they have also been rendered defective and/or strained by the grinding, since dehydroxylation occurs at lower temperatures than in the unground material. Thermal treatment $<350^\circ\text{C}$ results in the formation of a completely X-ray amorphous phase, which is, however, different from the amorphous phase formed when unground gibbsite dehydroxylates at about 300°C ; the latter contains Al in tetrahedral and octahedral coordination only, whereas the amorphous product from ground gibbsite contains the additional NMR resonance at about 34 ppm. The relative occupancies of these three sites are very similar to those reported [4] for an ill-defined amorphous ρ - Al_2O_3 .
4. The higher-temperature reactions of both ground and unground gibbsite follows a similar sequence involving γ - Al_2O_3 but the ground material displays greatly enhanced reactivity, showing XRD evidence of γ - Al_2O_3 formation at 700°C and α - Al_2O_3 at 900°C . By contrast, the thermal transformations in unground gibbsite are more gradual, the γ - Al_2O_3 which first appears at 800°C giving way to a mixture of θ and α - Al_2O_3 at 1200°C . The formation of crystalline corundum is complete at about 400°C higher than in the ground material. The high-temperature thermal sequences observed in this study are not identical with those reported elsewhere for ground gibbsite [6,7], suggesting that the other factors such as the defects or impurities in the starting material, and the method of grinding, can significantly influence the results.

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