JOURNAL OF MATERIALS SCIENCE 27 (1992) 4614–4618

Pillared montmorillonite clay as a raw material for the synthesis of β′-sialon

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To control the SiO_2/Al_2O_3 ratio in a starting clay material for the synthesis of β′-sialon by the carbothermal nitridation process, montmorillonite was pillared with Al_2O_3. Conversions to sialon of pillared clay (31% Al_2O_3) and reference unpillared montmorillonite (18% Al_2O_3) have been compared. Pillared montmorillonite yielded a mixture of β′-sialon and various oxynitrides and oxycarbides of alumina as intermediate products. Pillared clay transformed faster during annealing than structural components of smectite alone. For the proper thermal treatment and clay/carbon ratio, both pillared and unpillared clays resulted in β′-sialon solid solutions.

1. Introduction

Clays are potential aluminosilicate raw materials for β′-sialon powders which can be synthesized through simultaneous high-temperature carbothermal reduction and nitridation processes. Naturally occurring aluminosilicates are inexpensive and offer the possibility of an economically favourable alternative to silicon nitride and related products of sialon type. In natural aluminosilicates there are at least two chemical components (precursors) which are intimately mixed.

Starting from Lee and Cutler [1], numerous studies of the carbothermal nitridation of clays have been published. Further studies describe sialons prepared from various species of clays, i.e. illite, kaolin, montmorillonites [2–5]. Parameters influencing the reaction rate and possible reaction mechanisms have been recognized in many studies [6–9]. Nitrides may be formed by heterogeneous gas–solid reactions and/or through the metal-silicide liquid phase by reaction between components of mixture and gaseous nitrogen.

The entire reaction can be expressed as

$$\begin{aligned}(6-z)\,SiO_2 + z/2\,Al_2O_3 + yFe_2O_3 + sTiO_2 + rC \\ + 0.5\,(8-z+s)N_2 \\ Si_{6-z}Al_zO_zN_{8-z} + 2/3\,yFe_3C + sTiN \\ + (r-2/3y)CO \qquad (1a)\end{aligned}$$

where z, y, and s are deduced from the composition of starting raw material; r is defined by the stoichiometry of the reaction for carbothermal reduction of the above oxides and is equal to

$$r = 1.5\,(8 - z + 2y + 4/3s) \qquad (1b)$$

The extent of reaction (conversion of components to products) to sialon is mainly controlled by temperature, nitrogen-flow, character and purity of raw materials including the carbon content of the clay/carbon mixture. Because there are gas–solid interactions in the system, size, distribution and interconnectivity of pores in pellets of the solid mixture are of great significance.

The SiO_2/Al_2O_3 ratio of clay raw material depends on the clay deposit and on raw-material processing. For a specific commercial type of clay this ratio has a fixed value, and therefore, z in sialon cannot be changed as needed for a desired property, such as milling properties of pellets, sinterability of powder, mechanical properties of final product, etc.

To control the SiO_2/Al_2O_3 ratio in starting material for the synthesis of β′-sialon by the carbothermal nitridation process, smectite was pillared with Al_2O_3. Conversions to sialon of the pillared clay material and the reference unpillared montmorillonite are compared in the present study.

2. Experimental procedure

2.1. Clay

A natural montmorillonite (STx-1) was used. This sample contains minor amounts of quartz and calcite. It was pretreated with sodium acetate solution buffered at pH = 5 to remove the $CaCO_3$ [10]. The sample, which is free of $CaCO_3$, was dispersed in deionized water with the help of a dispersing agent, sodium hexametaphosphate, and $< 2\,\mu m$ fraction was separated by centrifugation. The fractionated sample was saturated with Ca^{2+} and $CaCl_2$ was removed by multiple washings with deionized water. The chemical analysis of $< 2\,\mu m$ calcium montmorillonite is given in Table I.

2.2. Pillaring

About one-half of the above sample (in the wet state) was treated with an excess alumina-pillaring solution (50 ml/g clay) for 4 h at room temperature under constant stirring. After completion of the reaction, excess salt was removed by washing repeatedly with deionized water. The alumina-pillaring solution was

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prepared by diluting 50% aluminium chlorohydrol solution 20 times with deionized water. The aluminium chlorohydrol in aqueous medium yields large hydroxy-Al-polycations of the type $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ [11], which replace Ca^{2+} from the interlayer exchange sites of the montmorillonite. The exchanged hydroxy-Al polymeric cations, after calcination, were converted to immobile (or fixed) oxide pillars in the interlayers that prop the layers apart with subsequent loss of swelling and generation of permanent microporosity. These pillars were found to be stable at least up to 700 °C. The pillaring process will introduce a large amount of aluminium into the interlays of montmorillonite which will be in intimate contact with aluminosilicate structure. Further details of the preparation and properties of pillared clay can be found in Malla and Komarneni [12]. In Table I, the chemical analysis of alumina-pillared montmorillonite is compared with that of non-pillared calcium montmorillonite. The carbon mixtures with calcium montmorillonite will be designated MM and pillared samples PMM, hereafter.

Both MM and PMM samples were suspended in water and mixed (in an ultraturex mixer SD-45) with an appropriate amount of activated carbon (wet powder; 1.02 times the amount defined by Equations 1a and b; the excess 2% carbon is to compensate for the presumable reduction of MgO which is also present in the raw material). Here, it is noted, that the rheological properties (at the same concentration of solids) of suspensions used were quite different. While MM suspension provides characteristic plastic behaviour of montmorillonite–water systems, the PMM appears like a suspension of non-plastic fine solid particles only. After centrifugation and extrusion of pellets (3 mm diameter × 3 mm) both mixtures were dried at about 150 °C under a stream of flowing hot air. Dry pellets of MM mixture provide higher tap and volume densities compared with PMM mixture as shown in Table I. This is due to their different rheological behaviour.

2.3. Carbothermal reduction and nitridation process

Carbothermal synthesis was carried out in a graphite cylindrical reactor (24 mm diameter × 60 mm). The design of reactor allows nitrogen flow through a bed of pellets. The reactor was kept in a molybdenum wire-wound tubular furnace. Both ends of the furnace were lighted with gas after keeping the reactor along with a sample of nitrogen (dry grade, 99.999% pure) in the furnace tube. Temperature was measured by a B-type thermocouple, which was calibrated under the experimental conditions.

In a typical experimental run, a charge of nearly 5 g was treated in the reactor. The flow-rate of the nitrogen gas was kept at 0.25 $dm^3 min^{-1}$ (at 20 °C and 101 kPa); the heating rate to the desired temperature was approximately 15 $°C min^{-1}$. The furnace was held at the desired temperature from 1–11 h with an accuracy of ± 5°C, and then cooled at 10 $°C min^{-1}$ to 600 °C.

TABLE I Composition of raw material (wt%)

Oxides	Unpillared montmorillonite	Pillared montmorillonite
SiO_2	72.97	64.25
Al_2O_3	18.00	31.31
Fe_2O_3	0.93	0.87
TiO_2	0.10	0.11
K_2O	0.11	0.10
Na_2O	0.06	0.04
CaO	4.53	0.52
MgO	3.23	2.85
Si/Al (mol)	3.5	1.8
z	1.35	2.19
	Density of pellets ($kg m^{-3}$)	
Mixture with carbon		
Apparent density	1100	690
Tap density	780	450

2.4. Evaluation

The reacted material was weighed and analysed to determine the transformation, temperature, and time (TTT) dependence of the systems under study. The nitrogen content and unreacted (free) carbon content were determined by means of standard chemical procedures. Phase identification was performed with a Scintag (USA) powder diffractometer using nickel-filtered CuK_α radiation. A data base of XRD patterns [13] was used for identification.

From the analytical results for raw materials and stoichiometric Equation 1 for synthesis, the final sialon should have a z-value of 1.35 for unpillared and 2.19 for the pillared samples, respectively.

In the present study the extent of the reaction, α_i, is expressed as

$$\alpha_i = v_i/v_o \qquad (2)$$

where i designates nitrogen and carbon, v_i is the mole of reacted carbon or bound nitrogen based on 100 g raw mixture, and v_o is the total number of moles of carbon in 100 g raw mixture or moles of nitrogen theoretically bound in sialon formed by complete reaction from 100 g raw mixture (Equation 1).
Then

$$\alpha_N = (1 - w_{L,\tau})\, w_{N,\tau}/(1 - w_{L,S})\, w_{N,S} \qquad (3)$$

where w is the weight fraction of nitrogen, N, and weight loss, L, after τ h thermal treatment, $w_{N,S}$ and $w_{L,S}$ are the weight fractions of nitrogen and weight loss according to the stoichiometry of Equation 1, and

$$\alpha_c = [w_{c,\phi} - (1 - w_{L,S})\, w_{c,\tau}]/w_{c,\phi} \qquad (4)$$

where $w_{c,\phi}$ and $w_{c,\tau}$ are the weight fractions of carbon before and after thermal treatment.

3. Results and discussion

3.1. Transformation–time dependence at 1450 °C

Mixture MM resulted in a nearly amorphous product after 1 h annealing (Fig. 1a). There is only one peak of low intensity (within the 2θ interval indicated in Fig. 1) at the position of the main peak of silicon carbide and

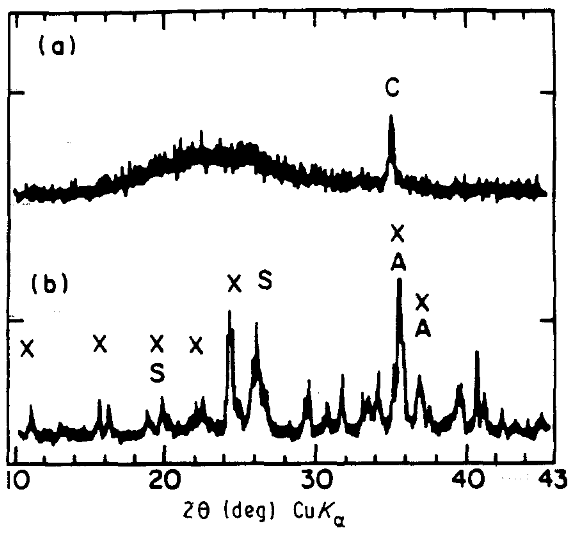

Figure 1 Phase evolution after 1 h thermal treatment at 1450 °C as determined by XRD: (a) unpillared mixture MM; (b) pillared mixture PMM. C = silicon carbide, X = X-phase, S = silicon oxynitrides, A = various aluminium oxynitrides (nAl$_2$O$_3$ · AlN), B = β′-sialon.

β′-sialon over the continuous diffraction background of amorphous phases. The different pattern of this sample is similar to another sample of MM which was heated for 6 h at 1350 °C.

Development of crystalline phases from the MM sample increased with reaction time. After 6 h treatment, there was no significant amorphous background. Crystalline β′-sialon, together with small portions of silicon and aluminium oxynitrides, were formed. The latter appears to have formed as a consequence of SiO loss from the pellets by means of transport through the gaseous phase. Owing to the loss of SiO, some regions remain locally richer in the aluminium component, and in the course of the reaction, higher aluminous oxynitride phases like phase X, J, ϕ and 15R, formed in these regions. Silicon-rich oxynitride phases, mainly Si_2ON_2, O′ phase and silicon dioxide formed as a fibrous felt on the surface of the pellets. This felt was poorly crystallized and consisted mainly of silicon, oxygen and nitrogen. Weight loss upon thermal treatment, the content of bound nitrogen and residual carbon, as well as the extent of reaction at 1450 °C, are summarized in Table II.

The PMN mixture transformed to a mixture of crystalline phases with little or no amorphous product after 1 h treatment at 1450 °C (Fig. 1b). From the XRD patterns, the X-phase, silicon oxynitride, aluminium oxynitrides and the low amount of β′-sialon and silicon carbide were identified (Fig. 1b). This result is in contrast with the MM mixture, which yielded mainly an amorphous product (Fig. 1a).

After 6 h annealing, the PMN samples yielded mainly β′-sialon (peaks of high intensity), ϕ phase and siliconoxynitrides as minor phases. The formation of aluminium oxynitride carbides of type $(Al_2OC)_{1-x} \cdot (AlN)_z$ is not conclusive, because the XRD peaks of the above phases overlap with these phases. However, the relatively high integral intensity of peak at $d = 0.241$ nm compared with those of peaks at 0.274, 0.251, 0.156, and 0.131 nm suggests the possible presence of aluminium oxynitride carbide. As can be seen from the results in Table II, the nitrogen content is higher while the carbon content is lower in the pillared samples compared to the unpillared counterparts. The presence of low-nitrogen phases of type $(Al_2O_3)_{1-n} \cdot (AlN)_n$, i.e. ϕ phase and silicon oxynitride phases, without any free carbon in the PMM sample after 6 h reaction time, suggests that there is a shortage of carbon in this reaction mixture. Therefore, another PMM mixture was prepared. This mixture is designated as corrected pillared montmorillonite mixture with carbon (CPMM) and contains 6% surplus carbon over the required stoichiometric amount. The CPMM samples resulted in crystallites of β′-sialon at 1450 °C after 6 h thermal treatment. There are substantially less intense peaks of minor phases compared with the PMM and MM mixtures. From chemical analyses it follows that both nitrogen and carbon conversions are complete (Table III, Fig. 2).

3.2. Thermal treatment at various temperatures

On increasing the temperature to 1490 °C, all the mixtures yielded β′-sialon (Fig. 3) as the main phase after 6 h annealing. There are, however, two unidentified peaks of low intensity (0.280 and 0.263 nm) in the MM mixture. The PMM sample still contained high amounts of aluminium oxynitride and minor amounts of aluminium–silicon–oxynitride phases. The CPMM mixture resulted in β′-sialon with traces of ϕ phase and silicon oxynitride. The β′-sialon obtained from MM and CPMM mixtures after annealing at 1490 °C

TABLE II Extent of reaction after thermal treatment of samples at 1450 °C for 1–6 h. (MM, unpillared montmorillonite with carbon; PMM, pillared montmorillonite with carbon)

Temperature (°C)	Time (h)	Mixture	Chemical analysis: Weight loss (%)	Chemical analysis: C (%)	Chemical analysis: N (%)	Extent of reaction, α: α_N	Extent of reaction, α: α_C
1450	1	MM	30.44	16.38	3.13	0.140	0.397
	1	PMM	42.76	3.10	7.90	0.335	0.900
	3	MM	35.5	6.88	7.59	0.315	0.765
	3	PMM	47.20	< 0.5	14.80	0.578	> 0.99
	4.5	MM	40.11	2.21	11.64	0.449	0.930
	4.5	PMM	48.09	0	19.56	0.751	1.0
	6	MM	43.11	0	15.46	0.566	1.0
	6	PMM	49.50	0	31.81	0.815	1.0

TABLE III Extent of reaction after thermal treatment of mixtures at different temperatures. (MM, unpillared montmorillonite with carbon; PMM, pillared montmorillonite with carbon; CPMM, pillared montmorillonite with higher carbon content)

Temperature (°C)	Time (h)	Mixture	Chemical analysis Weight loss (%)	C (%)	N (%)	Extent of reaction, α α_N	α_C
1490	6	MM	44.05	0	22.56	0.812	1.0
	6	PMM	51.0	0	23.63	0.857	1.0
	6	CPMM	53.6	0	26.52	1.0	1.0
1450	6	MM	43.11	0	15.46	0.566	1.0
	6	PMM	49.5	0	21.81	0.815	1.0
	6	CPMM	54.0	0	26.60	1.0	1.0
1410	6	MM	41.8	5.97	11.30	0.423	0.816
	6	PMM	48.8	0	18.90	0.716	1.0
1350	6	MM	37.5	10.12	8.82	0.355	0.665
	6	PMM	47.3	1.48	13.05	0.509	0.956
	6	CPMM	52.4	4.84	14.6	0.589	0.897
1350	11	MM	40.8	4.09	12.04	0.459	0.872
	11	PMM	48.12	< 0.5	16.23	0.623	> 0.99
	11	CPMM	55.2	1.98	22.68	0.862	0.960

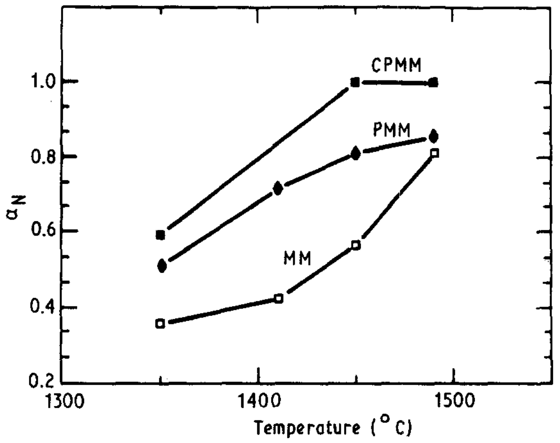

Figure 2 Nitrogen conversion, α_N, versus temperature after 6 h carbothermal nitridation; MM, unpillared mixture, PMM, pillared mixture; CPMM, pillared mixture with higher than stoichiometric content of carbon.

for 6 h may be considered as β′-sialon of technical purity (Fig. 3, Table III).

Samples of the MM mixture annealed at 1350 °C showed X-ray patterns of nearly amorphous products after 6 h. However, there was a broad background between 0.3 and 0.4 nm and low-intensity peaks appeared at the positions of silicon carbide main peaks (figure not shown). After heating for 11 h at 1350 °C, the peaks of silicon oxynitride, carbide, β′-sialon, X and J phases began to appear in the diffraction patterns (Fig. 4).

While the above unpillared samples resulted in only poorly crystalline material, the pillared material (PMM, CPMM, after 6 h) transformed to mixtures of crystalline phases with a small amount of amorphous component as indicated from the background readings. After 11 h annealing, the diffraction pattern indicates that the main diffracting species present are oxynitrides of aluminium and silicon (phases ϕ, O′ and X, which are transient products in the course of synthesis). The PMM samples contained only very small amounts of β′-sialon, whereas samples of CRMM mixture contained large amounts of β′-sialon together with minor amounts of silicon and aluminium oxynitrides (Fig. 4).

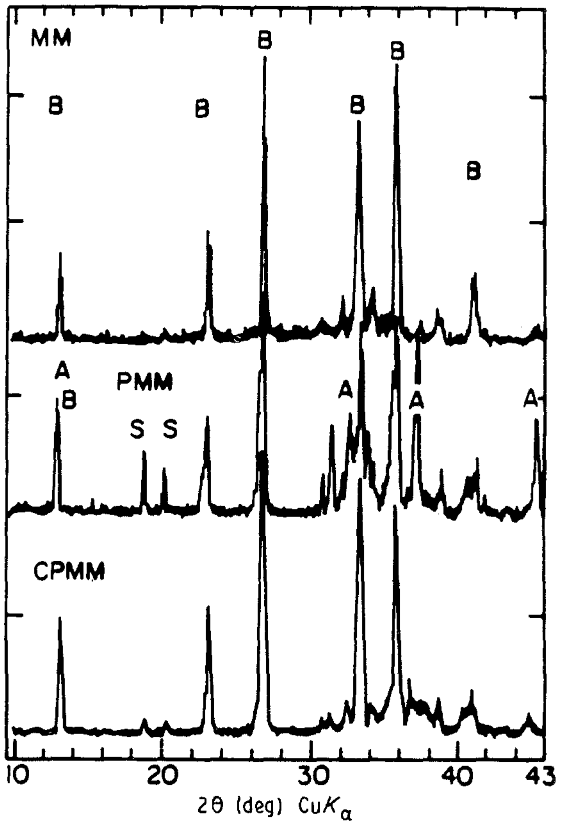

Figure 3 XRD powder patterns of samples treated at 1490 °C for 6 h; MM, unpillared mixture; PMM, pillared mixture; CPMM, pillared and contains a slight excess of carbon, B, β′-sialon; A, various aluminium oxynitrides ($n\text{Al}_2\text{O}_3 \cdot \text{AlN}$); S, silicon oxynitrides.

The transformation behaviour of samples treated at 1410 °C for 6 h is similar to those treated at 1350 °C for 11 h and 1450 °C for 4.5 h (Tables II and III).

The observed differences in reaction behaviour of the pillared and unpillared materials can be explained from the chemical and microstructural points of view. Pillars are the most reactive parts of a pillared smectite through the carbothermal nitridation treatment.

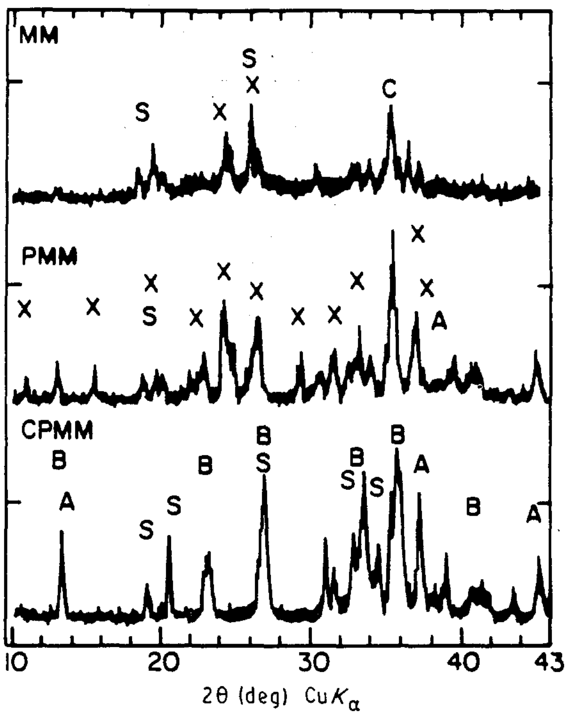

Figure 4 Comparison of XRD powder patterns of samples after thermal treatment at 1350 °C for 11 h. C, silicon carbide; S, silicon oxynitrides; A, various aluminium oxynitrides ($n\mathrm{Al_2O_3}\cdot\mathrm{AlN}$); B, β′-sialon; X, X-phase.

Aluminium oxynitrides and oxycarbides form from alumina pillars at the beginning of the reaction. This initial reaction of alumina pillars with carbon and nitrogen to form intermediate products occurs at a relatively lower temperature than the reaction of smectite itself. The enhanced reactivity of pillared samples can be attributed to the much higher surface area (300–400 $\mathrm{m^2\,g^{-1}}$) of these samples compared to the unpillared ones (30–50 $\mathrm{m^2\,g^{-1}}$) [14, 15]. The highly microporous nature of pillared samples facilitates easier diffusion of gaseous reactants (and intermediates) and hence enhanced reactivity. Only after longer reaction times and/or at higher temperatures do chemical and phase homogenization to sialon take place. Consumption of residual carbon and carbides to bond further amounts to nitrogen is characteristic of this stage.

While unpillared montmorillonite yielded β′-sialon at about 1450–1490 °C, a reaction temperature of about 1400 °C was enough for pillared samples with a slight excess of carbon over the stoichiometric clay/carbon ratio. The densification of sintered samples and the nature of their porosity as affected by the rheological properties of suspensions of raw clay materials are of great importance and need further study.

4. Conclusions

β′-sialon powders may be prepared with a range of z-values from pillared smectites. The reactivity of pillared smectites is different from that of unpillared smectite in two ways: (a) pillared samples yielded significantly greater amounts of aluminium oxynitride species in intermediate products, and (b) the reaction kinetics are faster in the pillared smectites apparently due to higher surface area and microporosity which facilitate faster diffusion of gaseous reactants. This study indicates that the aluminium component of pillars transformed faster during the thermal treatment than the structural components of smectite itself.

The present work clearly demonstrates that the pillaring process helped to control the $\mathrm{SiO_2/Al_2O_3}$ ratio of raw smectite material for the carbothermal nitridation process, and β′-sialon can be synthesized from pillared clay at a significantly lower temperature (about 50–100 °C) than from unpillared material.

Acknowledgement

This research was supported by the US Department of Energy under Grant no DE-FG02-85ER45204.

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Received 26 April
and accepted 2 August 1991