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Investigating the Properties of the Nanocomposite (poly(4-vinyl pyridine)/Al-SBA-15): A Precursor for β-SiAlON

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The nanocomposite precursor (P4VP/Al-SBA-15) was synthesized and then fired under N_2 atmosphere at 1450°C with 10°C/min heating rate and soaking time of 0 and 6 h in order to form β-SiAlON by using the carbothermal reduction and nitridation process (CRN). The nanocomposites was characterized by small-angle XRD (SXRD), microstructure studies (TEM/DSC) and ^{27}Al-NMR (MAS-NMR). Results, from the sample fired under N_2 atmosphere, showed that not only the carbon amount, type of carbon and the surface area of the precursor was important, but that a higher than stochiometric amount of carbon was unavoidable.

Keywords β-sialon; Al-SBA-15; carbothermal; nanocomposite; reduction

Introduction

Sialon ceramics are interesting candidate materials for various applications especially at high temperature. β-SiAlON, one of the most important forms of sialon, is a solid solution of β-Si_3N_4, with the replacement of Si and N, by Al and O [1], and has a general formula of: ($Si_{6-z}Al_zO_zN_{8-z}$), (0< Z <4. 2) [2–3]. β-SiAlON is a material that has high strength, good thermal-shock resistance, resistance against corrosion and erosion, and is superior to silicon nitride with respect to sinterability and oxidative resistance [4–6]. β-sialon powder can be synthesized from mixed powders of kaolinite, SiO_2-Al_2O_3. $2H_2O$ [7], SiO_2-Al_2O_3 [8–9], SiO_2-Al_2O_3-gel and a montmorillonite-polymer intercalation compound. All the above processes were conducted in the presence of carbon powder or carbon from the dissociation of a polymer under nitrogen (Carbothermal Reduction and Nitridation (CRN) method). In general, the CRN method occurs at temperatures higher than 1350°C [10–11].

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Due to the difficulty in controlling the elemental compositions of the Si/Al ratio in the raw materials, it is difficult to obtain products with different z-values. New methods are still required in order to synthesize high purity β-Sialon powders, with various z-values [12].

The mesoporous silica, SBA-15, with large pore size (normally 4–6 nm) and high surface area, has been widely studied [13]. Because of SBA-1's pore structure, carbon and aluminum can be easily be introduced into its nanosized channels [14]. Hence, we could obtain good powder mixtures of SiO_2–Al_2O_3–C, that were well-proportioned at the nanoscale, by impregnating the carbon and aluminum species into the channels of the SBA-15. Moreover, it was possible to accurately adjust the Si/Al ratios in the SiO_2–Al_2O_3–C composites by controlling the nanocasting procedure [15].

In this research, the nanocomposite (P4VP/Al-SBA-15), with Si/Al ratio equal to 1.66 that was suitable to form, β-SiAlON with z = 2. 25, was synthesized by using the CRN method. Results showed that not only the carbon amount, type of carbon and the surface area of the precursor were important factors, but that a higher than stochiometric amount of carbon was unavoidable during the nitridation process.

Experimental Procedure

Raw Materials

Tetraethyl orthosilicate (TEOS), aluminium isopropoxide, triblock copolymer pluronic ($PEO_{20}PPO_{70}PEO_{20}$, P123), H_3PO_4, monomeric 4-vinyl pyridine and benzoylperoxide was obtained from MERCK, ALDRICH, FULUKA, ACROS companies and used as received.

Instruments and Characterization

X-ray powder diffraction patterns were collected on a Philips PW 1700 computer-controlled goniometer with a graphite monochromator and SXRD, (D8ADVANCE, Germany) using a Cu Kα radiation system with a Ni filter. Transmission Electron Microscope (TEM) (Jeol model jem 2011) was evaluated along with the Energy Dispersive Spectroscopy (EDS) system. ^{27}Al (MAS-NMR) spectroscopy was carried out (11. 7T) on a BRUKER advance 500 spectrometer and 4 mm Doty MAS probes spun at approximately 10–12 kHz for the ^{27}Al spectra with respect to $Al(H_2O)_6^{3+}$.

Synthesis of Samples

Synthesis of Al-SBA-15. The hexagonally ordered Al-SBA-15 mesoporous silica-alumina structure was synthesised first. In a typical synthesis, Pluronic123 ($PEO_{20}PPO_{70}PEO_{20}$, P123) (2 g) [8], was dissolved in H_3PO_4 (4. 16 mL; 85%) and deionized water (75 mL). The solution was stirred at room temperature. Aluminium isopropoxide (1.58 g; 7.747 mmol) and tetraethyl orthosilicate (TEOS) (2. 86 mL; 0. 0129 mol) was added to the solution and stirred at 35°C for 24 h and then heated to 95°C and stirred for a further 24 h. The solution was filtered, washed with deionized water and dried in on oven at 95°C for 12 h. The product was finally calcined in two steps, firstly at 250°C for 3 h followed by 4 h at 550°C.

Synthesis of nanocomposite (poly 4-vinyle pyridine/Al-SBA-15). 4-vinyl pyridine (0.5 mL; 4.64 mmol), benzoylperoxide (0.034 g; 0.14 mmol) as initiator, Al-SBA-15 powder and tetrahydrofuran (THF) (7 mL) were added to a 50 mL round-bottom flask. The solution

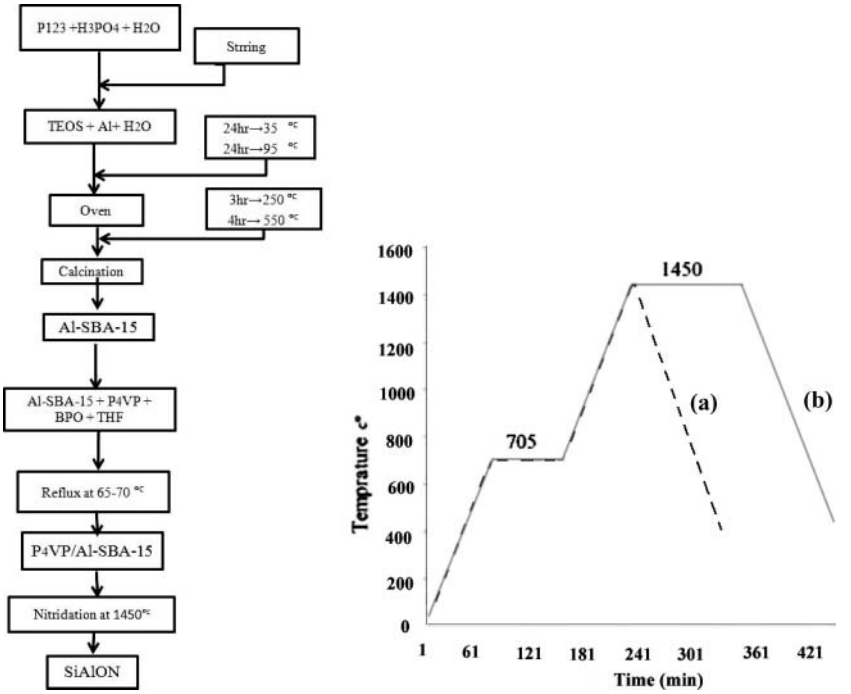

Figure 1. Schematic process of sialon synthesis from nanocomposite P4VP/Al-SBA-15 precursor with firing schedule and a heating rate of (10°C/min), a) without soaking time, b) with a soaking time of 6 h.

was stirred and refluxed for 5 h at 70°C. The solution was filtered, washed with THF and dried in air, to obtain the (P4VP/Al-SBA-15) nanocomposite powder.

Synthesis of β-SiAlON. The nanocomposite (P4VP/Al-SBA-15) powder was fired in a tube furnace under N_2 atmosphere at of 1450°C with a heating rate of 10°C/min, soaking time of 0 and 6 h and nitrogen flow of about 20 mL/min in order to form β-SiAlON. A schematic process of the sialon synthesis from the nanocomposite P4VP/Al-SBA-15 precursor, along with the firing schedule is shown in Fig. 1.

Results and Discussion

X-ray Diffraction

Figure 2 shows the small-angle x-ray diffraction patterns (SXRD) of the SBA-15 and Al-SBA-15 precursors. The XRD patterns of the materials showed three reflections, at 2θ values between 0.5^o – 3.0^o, This includes a strong peak (100) at 1 2^o and two weak peaks (110) and (200) at 1.9^o and 2.2^o respectively. This corresponds a highly ordered hexagonal mesoporous silica framework [16] and a two dimensional (2D) hexagonal mesostructure with space group *p6mm*. The XRD results showed that the order of the SBA-15 structure deteriorated with the addition of Aluminium. The presence of the peak (100) in the Al-SBA-15 spectrum, showed the mesoporous structure, but with the peak intensities, line width and disappearance of the (110) and (200) reflections, it could be related to a decrease in crystallinity.

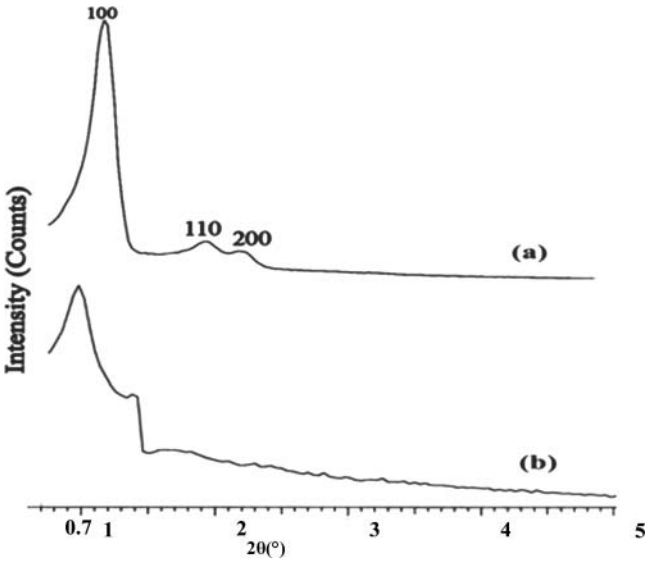

Figure 2. The powder XRD patterns of a) mesoporous silica SBA-15 and b) Al-SBA-15.

Specific Surface Area of Al-SBA-15 and the P4VP/Al-SBA-15 Nanocomposite

The structural properties are given in Table 1. It could be observed that with the addition of the polymer to the Al-SBA-15 precursor, the specific area decreased from 173.3 m^2g^{-1} to 61.95 m^2g^{-1} and the pore diameter decreased from 2.4 nm to 1.8 nm. This could be related to the filling of the hexagonal pores in the Al-SBA-15 structure during the polymerization process of 4-vinyle pyridine.

TEM Microstructure of Al-SBA-15 Precursor and the P4VP/Al-SBA-15 Nanocomposite

The mesostructures of SBA-15 and Al-SBA-15 were confirmed by TEM studies. The TEM images of Al-SBA-15 perpendicular and parallel to the pore axis are given in Figs. 3(b) and 4. The results showed that the hexagonal ordered pore structures, after incorporation of Al into the structure of SBA-15, had changed and it seemed that the ordering level had decreased.

Figure 4 shows the TEM image parallel to the pore axis of the Al-SBA-15 precursor. It showed that the hexagonal pore diameter in Al-SBA-15 was approximately 20 nm.

Table 1. Structural parameters of Al-SBA-15 and nanocomposite P4VP/Al-SBA-15 precursors

Sample	BET surface area (m^2 g^{-1})	V_P (cm^3 g^{-1})	D_P (nm)
Al-SBA-15	173.3	0.0604	2.4
P4VP/Al-SBA -15	61.95	0.0188	1.8

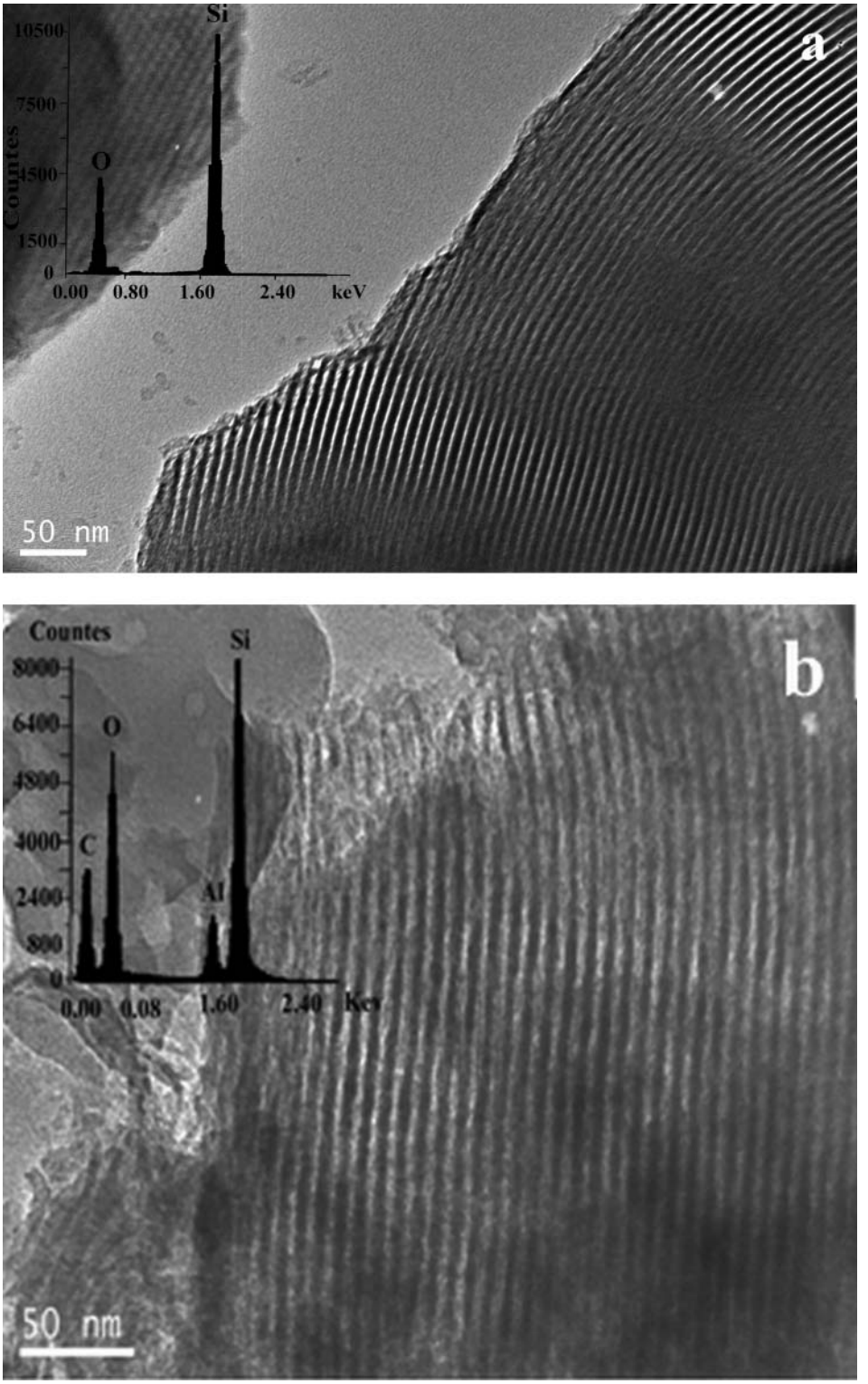

Figure 3. TEM/EDS images perpendicular to the pore axis a) SBA-15 and b) Al-SBA-15.

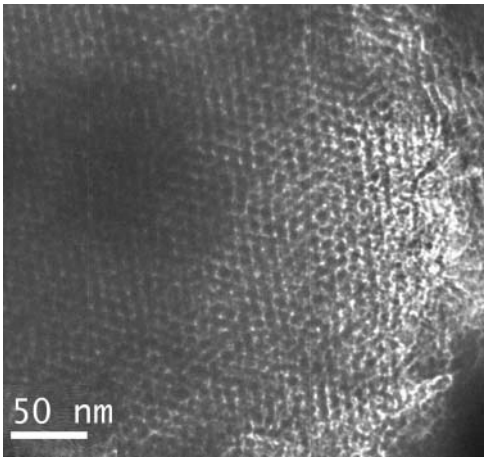

Figure 4. TEM image of Al-SBA-15 precursor parallel to the pore axis.

^{27}Al (MAS-NMR) Spectra

The ^{27}Al (MAS-NMR) spectra of Al-SBA-15 and the P4VP/Al-SBA-15 nanocomposite is shown in Fig. 5. A strong peak at 40.9 ppm, assigned to tetrahedral Al, and a weak peak at -14.8 ppm, attributed to the octahedral Al, could be observed. The results confirmed the presence of Al in the Al-SBA-15 and P4VP/Al-SBA-15 nanocomposite structure.

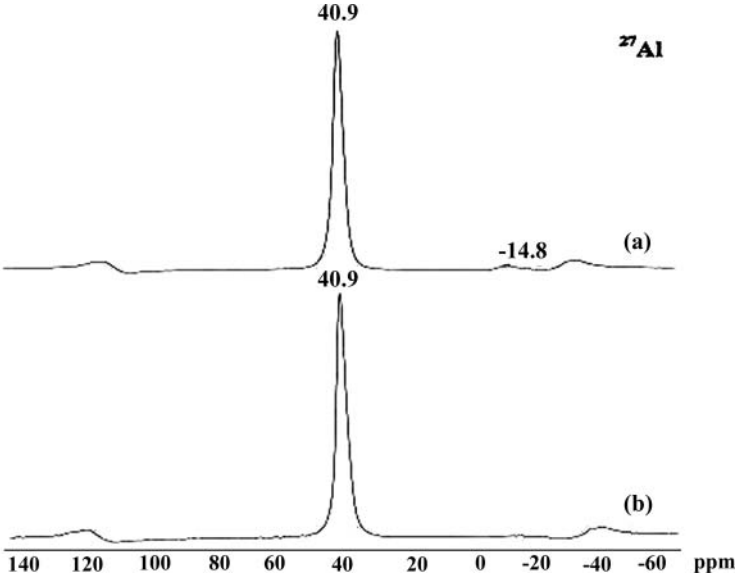

Figure 5. ^{27}Al-MAS-NMR, of a) Al-SBA-15 and b) P4VP/Al-SBA-15 nanocomposite, chemical shift (ppm) w.r.t $Al(H_2O)_6^{3+}$.

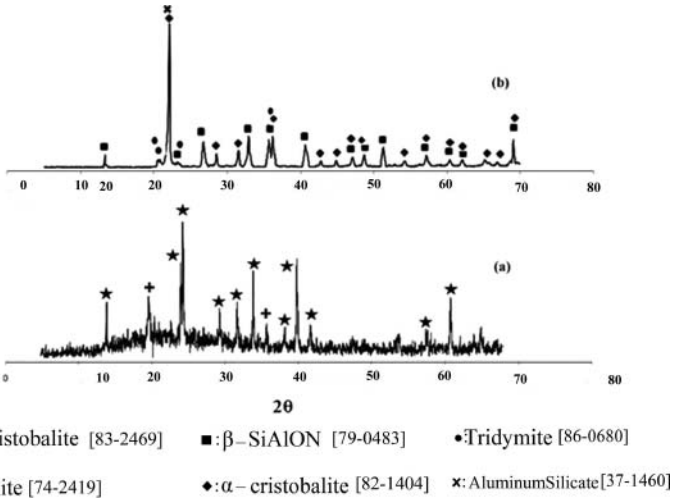

Figure 6. X-ray diffraction patterns of the P4VP/Al-SBA-15 nanocomposite, heated in a nitrogen atmosphere at 1450°C, a) with soaking time of 0 h (Co lamp) and b) soaking time of 6 h (Cu lamp).

Phase Analysis of Nitrified Samples

The X-ray diffraction pattern of the P4VP/Al-SBA-15 nanocomposite at 1450°C without soaking is shown in Fig. 6. The XRD analysis showed that without soaking at 1450°C, the mullite phase was present, which confirmed that the Si/Al ratio used was correct. By soaking at 1450°C for 6 h, the Aluminum-silicate phase (JCPDS number :37-1460) and β-SiAlON (JCPDS number: 79-0483) were formed.

Conclusions

From this study it was observed that by incorporating Al into the SBA-15 structure, the ordering level was decreased. Also, the mesoporous structure of Al-SBA-15 was confirmed by TEM studies and ^{27}Al (MAS-NMR) studies proved the presence of Al-SBA-15 in atomic scale. Finally, to form the nitride phase during nitridation process not only the amount carbon, type of carbon and surface area of precursor were important factors but also a higher amount of carbon than stoichiometric amount was unavoidable.

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