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Synthesis Of Pentacoordinate Organic Silicon And Polyphosphazene Containing Silicon With Hydrophobic Superfine SiO_2

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ABSTRACT

Pentacoordinate organic silicon was prepared with a new material of hydrophobic superfine SiO_2 at a much shorter reaction time and higher yield, and then it was used to react with hexachlorocyclotriphosphazne to get polyphosphazene containing silicon, the products behavior was studied with TGA and infrared spectrum.

KEYWORDS

Hexachlorocyclotriphosphazne;
Pentacoordinate organic silicon;
Synthesis;
Thermogravimetric analysis.

INTRODUCTION

Silicon is one of the most abundance natural resources, which is very important to develop organic materials containing silicon. But the organosilicon monomers involved in these approaches are prepared exclusively from carbothermal reduction of silicon dioxide which is energy-extensive and equipment-extensive[1]. Pentacoordinate silicon can be prepared directly from SiO_2 and ethylene glycol in the presence of KOH at about 200^0C was firstly reported by Laine et al in 1991[2],which have received extensive attention in the last decades. It has opened up many avenues for new research in the fields of conductor materials and high-performance ceramics overseas[3-5], and the polymers containing silicon was successfully used to the surface modification of silica white and synthesis of polyurethane containing silicon in recent years at home[6].

In this paper, pentacoordinate organic silicon was prepared with a new material of hydrophobic superfine SiO_2, then it was used to react with hexachlorocyclotriphosphazne to get polyphosphazene containing silicon, and the products behavior was preliminarily studied with TGA and infrared spectrum.

EXPERIMENTAL

Materials

Hydrophobic superfine SiO_2 was industrial grade obtained from Tianjin Yuli chemical technology plant. The other reagents of glycol, potassium hydroxide, absolute methanol, chlorobenzene, pyridine, phosphor pentachloride and dioxane were all analytical grade.

Synthesis

1. Synthesis of hexachlorocyclotriphosphazne

The synthesis of hexachlorocyclotriphosphazne was according to the reference of[7,8].

2. Synthesis of potassium glycolate silicate

The synthesis of potassium glycolato silicate was according to the reference of[2,9,10].

3. Synthesis of polyphosphazene containing silicon

The synthesis of polyphosphazene containing silicon was according to the reference of[9,10].

Analysis methods

1. IR spectrum

Samples were analyzed by fourier transform after potassium bromide tabulating on Vertor27 (Bruker).

2. Thermogravimetric analysis

Thermogravimetric analysis was performed at 20^0C/min on WCT-2 differential thermal analyzer under N_2.

3. XRD

X-ray diffraction (XRD) analysis was performed at 20^0/min on D/MAX-II diffractometer equipped with graphite monochromatized Cu, the diffraction angle range is from 10^0 to 60^0.

RESULT AND DISCUSSION

Synthesis of pentacoordinate organic silicon and polyphosphazene containing silicon

1. Synthesis of pentacoordinate organic silicon

In a three necked bottle a mixture of 6.0 g Hydrophobic superfine SiO_2, 5.6 g KOH and 120 mL $HOCH_2CH_2OH$ was stirred magnetically under N_2 for ten minutes, and then was heated to about 200^0C, standard distillation setup so that all the excess glycol was distilled off slowly with removal of water, after thirty minutes solid product was appearing and then stopped the reaction. The solid product was kept sealing overnight and then dissolved with 100mL CH_3OH and filtered. The filtrate was precipitated with 400 mL CH_3CN, the precipitate was dried at 130^0C in vacuum, the yield is about 90%.

2. Synthesis of polyphosphazene containing silicon

Hexachlorocyclotriphosphazne was recrystallized from n-heptane several times before use. 3.47 g HCCP was dissolved in 10 mL dioxane and added dropwised into 60 mL solution of potassium glycolato silicate in methanol under reflexing in the presence of nitrogen. Then the mixture was agitated vigorously to react until the solution reached neutrality. The reaction mixture was filtered to remove the white precipiate and dried at 130^0C in vacuum . The obtained primrose powder was polyphosphazene containing silicon.

Structure analysis

1. XRD spectrum of the white precipitate

X-ray diffraction (XRD) analysis of the white precipitate and pure KCl in analytical reagent grade were performed. The results were shown in figure 1. Comparing (a) and (b), it is sure that the precipitate is KCl. Thus we can conclude that pentacoordinate silicon has replaced the chlorine in hexachlorocyclo-

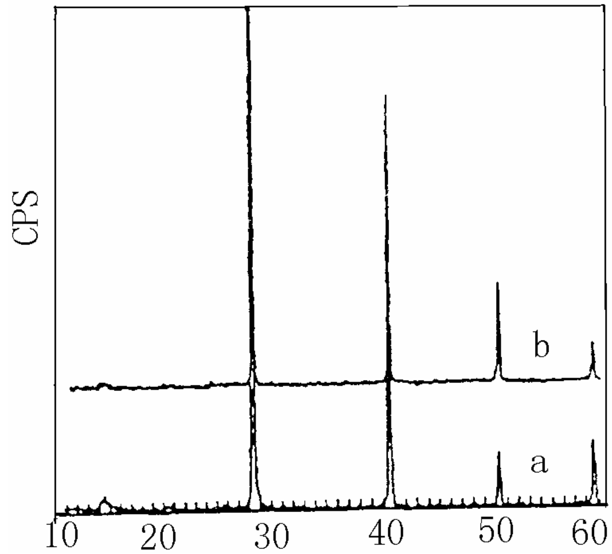

Figure 1: XRD spectrum (a) pure KCl (b) the white precipitate

triphosphazne.

2. IR spectrum of the product

Figure 2 is the IR spectrum of the product. In figure (a), the band at 3388cm^{-1} was caused by the vibration of OH$^-$ group, the band at 2855 cm^{-1} was assigned to the vibration of -CH$_2$- group, and the bands at 1093 cm^{-1} and 1040 cm^{-1} were attributed to Si-O-C group and the C-O group joining with -OH, the above data is consistent with the reference[9]. Comparing figure (b) with (a) and (c), we can find after reaction, the most strong absorption peaks of P=N shifted to higher wavenumber from 1169 cm^{-1} and 1215 cm^{-1} to 1331 cm^{-1}and 1425 cm^{-1}, the bands at 522 and 603 cm^{-1} attributed to the vibration of pCl group disappeared, the bands of Si-O-C and P-O-C overlapped at 1082 cm^{-1}. From the figure (b) we also find–CH$_2$-, the bands at 2952 cm^{-1} and 2860 cm^{-1} were assigned to the groups of -CH$_3$ and, the bands at 1082 cm^{-1} and 970 cm^{-1} were caused by the vibration of P-O-C group, the peak at 3418 cm^{-1} was attributed to the vibration of OH$^-$ group. From the above results we can conclude that pentacoordinate organic silicon has substituted the chlorine in hexachlorocyclotriphosphazne and some of silicons have connected to the phosphazene ring.

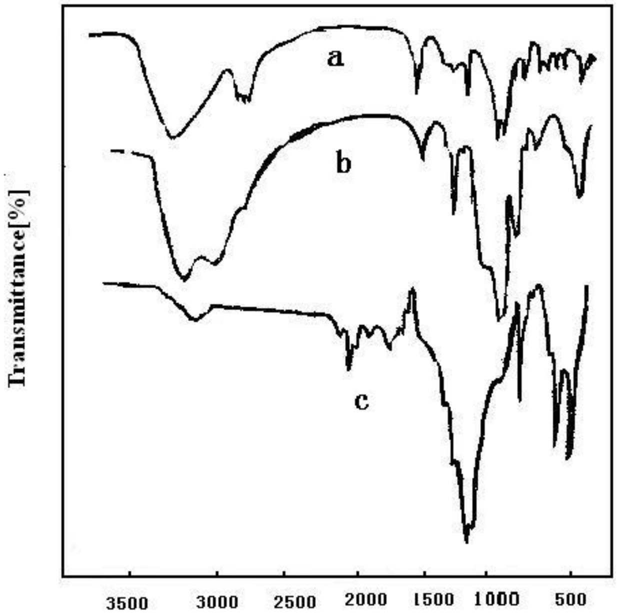

Figure 2: IR spectrum of the product (a) pentacoordinate organic silicon (b) polyphosphazene containing silicon (c) hexachlorocyclotriphosphazne

Thermogravimetric analysis of the product

Figure 3 shows the results of TG and TGA analysis of polyphosphazene containing silicon. There are three apparent mass loss processes .The initial 5.4% at 79.9^{0}C mass loss corresponds to the volatilization of small molecules such as methanol, dioxane and so on. The second mass loss period at about 253.8^{0}C is ascribed to the decomposition of the phosphazene ring to give off ammonia or the other nitride, and the amount of mass loss is 19%.The third mass loss is at 346.7^{0}C with the amount of mass loss 11%, this process corresponds to the carbonization of the residue. But the product will do on decomposing and losing until 711.3^{0}C, the ultimate residue of the product is 55.0%. This result is consistent with the report of Liu and Matyjaszewski[9-11].

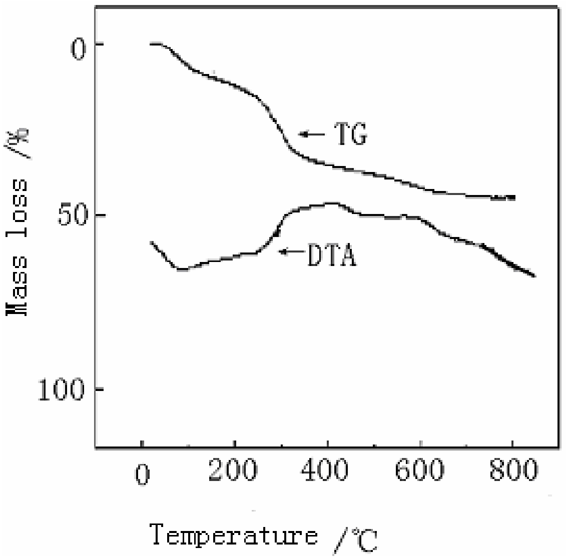

Figure 3: TGA of the product

CONCLUSIONS

Pentacoordinate organic silicon was synthesized with a new material of hydrophobic superfine SiO$_2$ at a much shorter time and higher yield comparing with that of silica. The obtained pentacoordinate organic silicon was reacted with hexachlorocyclotriphosphazne to get polyphosphazene containing silicon, the results of analysis of TGA show that the product has good thermal stability which can open up many avenues for new research in the field of flame retardants containing silicon.

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