

Preparation of L-Phenylalanine Polypeptide/SBA-15 Nanocomposites and Their Adsorbent Property

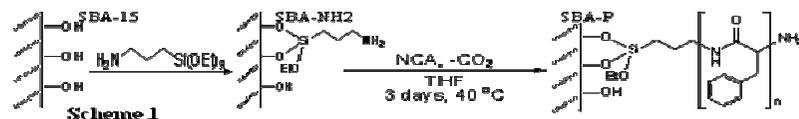
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Introduction

Mesoporous materials with high surface area and pore volume have attracted great attention during the past decade and have been widely used in separation processes or shape-selective catalysis. One of the main disadvantages of these materials is that they often have too large inner space to control the shape selectivity of the reactant molecules. To overcome this problem, organic functionalization of the inner space of mesoporous materials has been achieved by modifying the mesoporous silica surfaces with various silane coupling agents. In the present study we have attempted to modify the inner space of SBA-15 with L-phenylalanine polypeptide polymer chains, which were formed by the oligomerization of L-phenylalanine N-carboxyhydride on the grafted $-NH_2$ group sites inside the pore of SBA-15. The catalytic property of the obtained nanocomposites was evaluated by adsorptive separation of a racemic mixture of D- and L-phenylalanines.

Materials and Methods

L-phenylalanine polypeptide/SBA-15 nanocomposites were prepared by the following procedure summarized in Scheme 1. A toluene solution (15 mL) of 3 mL 3-amino-propyltriethoxysilane was added to 1 g of calcined SBA-15. The mixture was refluxed at 120 °C for 10 hrs. The obtained SBA-NH₂ was collected by filtration and washed with toluene and ethanol and dried at 80 °C. Then THF solution (15 mL) of NCA (N-carboxyanhydride) of L-phenylalanine was added to 0.1 g of the SBA-NH₂. The mixture was stirred for 3 days at 40 °C under inert atmosphere. The obtained SBA-polymer nanocomposite (SBA-P) was collected by filtration and washed with THF and dried at 80 °C.



Results and Discussion

Three kinds of L-phenylalanine polypeptide/SBA-15 were prepared with NCA/SBA-NH₂ weight ratio = 0.5, 1.0 and 2.0 (designated as SBA-P0.5, SBA-P1 and SBA-P2, respectively). The TG profiles of various samples are shown in Fig. 1(A). The weight loss by TG measurements under air was increased with the increased ratios of NCA/SBA-NH₂ as summarized in Table 1. In DTA profile, the decomposition of the SBA-NH₂ has only one exothermic peak at 563K, whereas SBA-P samples have three exothermic peaks at 620, 690

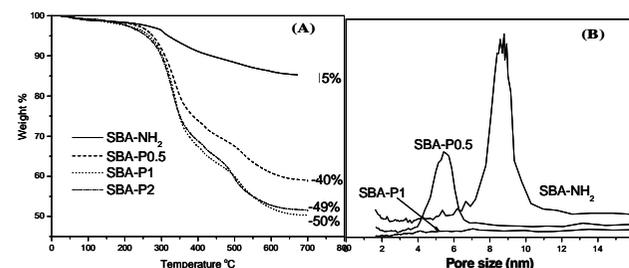


Fig. 1 TG(A) and pore size distribution(B) of various SBA nanocomposites

and 770K whose positions are different from that of SBA-NH₂ sample. These results clearly indicate that polymerization initiated at the modified NH₂ group. On the other hand, the weight losses were similar between the samples SBA-P1 and SBA-P2, indicating that once silica-pore was filled with the polymer chains, no more polymerization took place. The pore size distribution estimated from N₂ sorption isotherms are shown in Fig. 1(B) and their pore parameters are summarized in Table 1. The pore size and BET surface area both decreased after the polymerization. For the SBA-P0.5 sample, the pore size was 5.5 nm, whereas there were no pores remained in the SBA-P1 sample. From the pore volume data, the polymer occupied volume can be estimated as follows; $0.677 - 0.245 = 0.432 \text{ cm}^3/\text{g}$ for SBA-P0.5 sample and $0.677 - 0.052 = 0.625 \text{ cm}^3/\text{g}$ for SBA-P1 sample. By assuming that the densities of polymers in these two samples are the same, the weight ratio of the polymers in these two can be estimated as $0.432/0.625 = 0.691$. From the TG data, the weight ratio of polymers between these two samples is $(40-15) / (50-15) = 0.714$. By comparison with these two ratios, it is reasonable to suppose that the polymerization takes place only inside the pore. If we assume that all the grafted NH₂ groups (1 to 2 units per 1 nm² of SBA-15) can initiate the polymerization reaction, the phenylalanine unit (n) in the formed oligomers was estimated to be three to four.

The adsorbent property of SBA-P0.5 sample was evaluated by adsorptive separation of racemic mixture of D- and L-phenylalanines and a few percent enantio excessive results were obtained.

Table 1 TG, DTA, SA and Pore-parameters of Polymer/SBA Nanocomposites

Sample	Weight loss by TG (%)	DTA peak position (K)	BET SA (m ² /g)	Pore Vol. (cm ³ /g)	Pore size (nm)
SBA-NH ₂	15	563	417	0.677	8.7
SBA-P0.5	40	620, 690, 770	154	0.245	5.5
SBA-P1	50	620, 690, 770	27	0.052	—
SBA-P2	49	620, 690, 770	—	—	—

Significance

L-phenylalanine polypeptide polymer was firstly prepared inside the pore of SBA-15, which showed the enantioselective adsorption property for phenylalanine molecules.