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Synthesis of Mesoporous Hollow Silica using NaA Zeolite as Sacrificial Cores and its Application for Anchoring the Chiral Catalyst

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Extended Abstract

Some recent research efforts have been paid to the synthesis of mesoporous materials with large pore sizes and uniform pore size distribution [2-4]. The hollow-type composites with well-defined mesostructures have been attracted a growing interest because of their potential applications in catalysis, chromatography, filler, and the protection of biologically active agent [1, 3]. Formation of porosity on the surfaces of inorganic support could be advantageous for a variety of applications. It is well known that chiral Co(III) salen complexes are very enantioselective for the asymmetric hydrolysis of terminal epoxides [3]. In this study, Hollow type mesoporous silica was synthesized using NaA Zeolite(NaA) as a template core. After removal of the NaA cores by hydrochloric acid, chiral Co(III) salen complexes were immobilized in the vacant cores through encapsulation treatment. First, 1.0 g of NaA was added into the ethanol(20ml), pure water (10ml) and ammonium hydroxide(3.14ml) then the mixture was stirred for 0.5h. Tetraethyl orthosilicate (TEOS) (5ml) and trimethoxy(octadecyl)silane (C18 silane) (0.4ml) was added dropwise into the mixture and rapidly stirred for 1.5h. By this treatment, mesoporous silica was coated on the surfaces of NaA. After filtration of solid product, it was calcinated at 550°C for 5h in air. The inorganic composite of mesoporous silica/ NaA was added into hydrochloric acid (35%) and it was stirred at 80°C for 48h. The aluminium component in NaA was leached out during the acid treatment, so that the inside of mesoporous walls became empty. Because the crystal structure of NaA is very weak in the strong acid solution, NaA, except hollow silica wall covered on it, was fully destroyed and dissolved in 35% HCl solution. The mesostructure of hollow silica was characterized by X-ray Diffractometer (DMAX-2500(Rigaku)), Fe-TEM (JEM-2100F) and SEM (Hitachi S-4300) analysis. Chiral Co(III) salen complex was encapsulated in the mesoporous hollow silica by the method reported in the previous paper [2]. The activities of heterogeneous chiral salen catalysts were examined in the hydrolytic kinetic resolution (HKR) of epichlorohydrin (ECH). The conversion and ee% values were determined by capillary GC equipped with chiral columns (HP-225 50% cyanopropyl). The mesoporous hollow silica could be fabricated so easily by sacrificial method using NaA, and the samples obtained in this work was efficient support for immobilization of chiral Co- salen complexes. Those heterogenized chiral catalysts have shown the very high reactivity in HKR of terminal epoxides.

Deng, Z., Chen, M., Zhou, S., You, B., & Wu L. (2006). A Novel Method for the Fabrication of Monodisperse Hollow Silica Spheres. *Langmur*, 22, 6403-6407.

- Kim, S.H., Shin, C.K., Ahn, C.H., & Kim, G.J. (2006). Syntheses and Application of Silica Monolith with Bimodal Meso/Macroscopic Pore Structure. *J. Porous Mater.*, 13, 201-205.
- Schmid, A., Fujii, S., & Armes, S.P. (2006). Polystyrene-Silica Nanocomposite Particles via Alcoholic Dispersion Polymerization Using a Cationic Azo Initiator. *Langmur*, 22, 4923-4927.
- Yang, H., Li, J., Yang, J., Liu, Z., Yang. Q., & Li, C. (2007). Asymmetric Reactions On Chiral Catalysts Entrapped Within A Mesoporous Cage. *Chem. Comm.*, 1086-1088.
- Yuan, Q., Hagen, A., & Roessner, F. (2006). An Investigation into the Ti-Grafting Structure on MCM-41 and Epoxidation Catalysis. *Appl. Catal. A: Gen.*, 303, 81-87.