

Preparation of Chemically Active Mesoporous Adsorbent for Pt(II) and Pd(II) Adsorption from Aqueous Solutions

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Abstract—Chemically active mesoporous silica was prepared via grafting of N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole. Binding behavior of the adsorbent toward Pt(II) and Pd(II) ions was investigated. In addition, the properties of the adsorbent, such as pore structure and pore uniformity, were also examined. Results showed that the adsorbents developed in this study have high affinity for noble metal ions, such as Pt(II) and Pd(II), in aqueous solutions.

Key words: Imidazole, Mesoporous Silica, Adsorbent, Noble Metal Ion

INTRODUCTION

For metal extractions from dilute aqueous solutions, solid-phase adsorbents have greater applicability than traditional solvent extraction. A variety of adsorbents have been studied extensively for this purpose. Kim et al. [2000] and Chah et al. [2002] synthesized the adsorbent for heavy metal removal using silica. Adsorbents using hollow fibers have also been reported [Choi et al., 1999]. The recent discovery of mesoporous molecular sieves has stimulated a renewed interest in developing a novel adsorbent, since these materials show relatively large and uniform pore diameter with cylindrical pore shape. These properties are advantageous for use in aqueous solution because of tremendous reduction of diffusion resistance. For mesoporous materials to be used as an adsorbent, functional groups should be incorporated on the surface of these materials. A variety of functionalization methods of mesoporous materials such as grafting, co-condensation have been widely documented [Stein et al., 2000]. Liu and coworkers [1998] also prepared organic-inorganic hybrid mesoporous materials via coating method. Lee et al. [2001] prepared HMS type adsorbent for heavy metal removal. Dai and coworkers [2000] synthesized selective Cu²⁺ adsorbents using MCM type mesoporous silica. Brown et al. [1999] also reported that selective Hg²⁺ adsorbent could be synthesized by using silica.

However, little research has been reported for the adsorption of noble metal ions using mesoporous silica. Talanova et al. [2001] reported that polymeric extractants with heterocyclic amine units exhibited efficient adsorption of Pd(II) and Pt(II) from aqueous solutions, and Liu et al. [2002] reported that polymers containing functional groups with donor N and S atoms were the promising adsorbents toward noble metal ions. In this study, mesoporous adsorbents functionalized with chelating ligand (imidazole group) via grafting method were synthesized and applied for the adsorption of noble

metals in aqueous solutions. To our knowledge, this work, is the first attempt to develop functionalized mesoporous silicas for noble metal ion adsorption.

EXPERIMENTAL

SBA-15 mesoporous silica was synthesized by using a non-ionic surfactant, Pluronic P123 (poly(alkylene) oxide triblock copolymer, BASF Co.) as a template and tetraethylorthosilicate (TEOS, Aldrich Chemical Co.) as a silica precursor. In a typical experiment 10.0 g of Pluronic P123 was dissolved in an aqueous HCl solution (1.6 M, 358 ml). TEOS, 14.3 g, was added to this solution and the mixture was stirred vigorously, which resulted in a microemulsion. After 20 hr, this perfectly transparent solution was heated to 100 °C and maintained for 24 hr with stirring. The resulting solid, SBA-15, was filtered off and washed. The surfactant was then removed by hot ethanol extraction in a Soxhlet apparatus. In order to graft metal adsorptive functional group containing silane on the mesopore wall, SBA-15 was silanized with N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (Imidazole, Gelest Inc.). In the specific synthesis of imidazole grafted SBA-15 (Imi-SBA-15), 2.0 g of SBA-15 was refluxed with 3 ml of imidazole in 60 ml of dry toluene for 20 hr. Solid products were filtered off and washed with solvents in the order of toluene, acetone and ethanol. Elemental analysis was conducted by elemental analyzer (RECO CHNS-932). N₂ adsorption-desorption isotherms were measured with a sorptometer (ASAP 2010, Micromeritics Co.). Fourier transform infrared spectroscopy (M2200, Midac Co.) was used to identify the functional groups in the samples. Small-Angle X-ray Scattering (SAXS) patterns were collected on a Bruker GADDS diffractometer.

A batch technique was applied to determine the metal binding capacity of as-synthesized adsorbents. Typically, 0.1 g of adsorbent was equilibrated with 10 mL of 1 mM K₂PtCl₆ or K₂PdCl₆ (pH 4 buffer) in stoppered plastic vials; this mixture was shaken for 12 hr and the concentration of metal ion in the supernatant solution was analyzed by using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES).

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‡This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

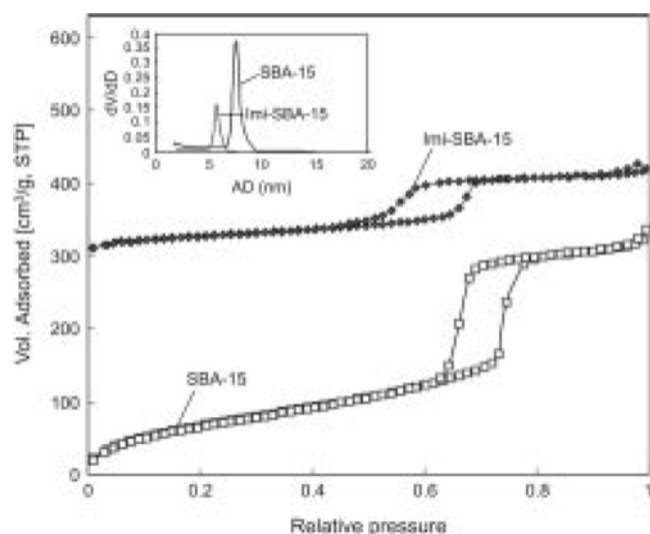


Fig. 1. N_2 adsorption-desorption isotherms of SBA-15 and Imi-SBA-15 prepared by grafting method. BJH pore size distribution obtained from the desorption branch are included for comparison (inner figure).

RESULTS AND DISCUSSION

Fig. 1 shows N_2 adsorption/desorption isotherms of SBA-15 and imidazole grafted SBA-15 (Imi-SBA-15). Two samples showed irreversible type IV adsorption isotherms with a H1 hysteresis loop as defined in the IUPAC. Surface area, pore diameter and pore volume of SBA-15 decreased due to the grafting of imidazole. Pore size distributions of SBA-15 and Imi-SBA-15 were similar except for the average pore diameter, which decreased approximately 2 nm because of grafting. Hexagonal mesoporous structure of SBA-15 was not altered through the preparation steps. These conservations of the mesoporous structure are confirmed more precisely by the SAXS data (not shown here). Regardless of surface treatments, two samples had the same primary peak at 0.83° , which implies the ma-

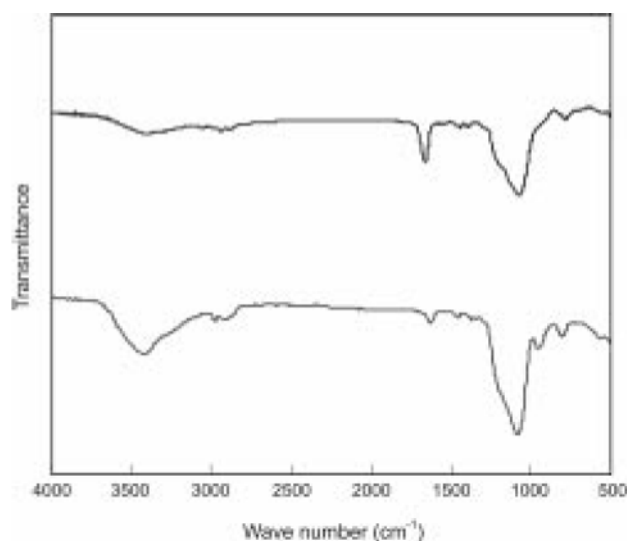


Fig. 2. FT-IR spectra of SBA-15 (lower spectra) and Imi-SBA-15 (upper spectra).

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Table 1. Noble metal ion adsorption using single metal ion solution at pH 4

Sample	Pt(II)			Pd(II)		
	Uptake (%)	K_d (ml/g)	Sorbed (mmol/g)	Uptake (%)	K_d (ml/g)	Sorbed (mmol/g)
SBA-15	20.89	26	0.019	13.51	15	0.012
Imi-SBA-15	99.38	15960	0.093	97.75	4337	0.093

terials prepared have an identical cell parameter with SBA-15. These results reflect that the silica mesostructure of relatively large and uniform pore size with cylindrical pore shape was conserved during the grafting. The functional groups contained by two samples were identified by using FT-IR (Fig. 2). O-H bond stretching bands of silanol groups were observed at $3,200\text{--}3,600\text{ cm}^{-1}$. Silanol groups on the silica surface exist as several types, such as isolated, hydrogen-bonded, and geminal types of silanol. The IR absorption bands of these silanol groups correspond to the peaks at $3,738\text{ cm}^{-1}$, $3,200\text{--}3,600\text{ cm}^{-1}$ and $3,738\text{ cm}^{-1}$. The results showed that the surface silanol group was mainly of the hydrogen-bonded type, in IR absorption bands which were observed at $3,200\text{--}3,600\text{ cm}^{-1}$. The siloxane, $-(\text{SiO})_n-$, peak broadly appeared at $1,000\text{--}1,100\text{ cm}^{-1}$. Si-O bond stretching was detected at 960 cm^{-1} . After grafting of imidazole, O-H bond stretching bands of silanol groups disappeared, while the adsorption bands at $1,544\text{--}1,734\text{ cm}^{-1}$ appeared due to the imidazole grafting [Socrates, 1994]. The amount of imidazole grafted in the adsorbent was calculated, based on N contents from an elemental analysis (not shown here) was 3.64 mmol/g SBA-15.

Metal adsorption experiments were performed by using SBA-15 and Imi-SBA-15 in buffer solution at pH 4. The amount of adsorbed metal ions is shown in Table 1. The extent of metal adsorption capability can be represented by distribution coefficient, K_d , which is defined as the ratio of the amount of metal ions in solid matrix to those in liquid matrix as listed in Table 1. The results showed that SBA-15 itself had a little binding affinity for Pt(II) and Pd(II) metals. Imi-SBA-15 exhibited much higher binding affinity for noble metal ions than other polymer-based adsorbents [Pd(II), Pt(II)] [Talanova et al., 2001], fiber-based adsorbents [Pd(II)] [Liu et al., 2002] reported in the literature.

In conclusion, we report here the synthesis of noble metal ion adsorbent using mesoporous silica, SBA-15. The surface of SBA-15 was functionalized by imidazole via grafting method. Some losses in surface area and pore volume occurred. However, ordered mesoporous structure of the support was conserved through the synthetic steps. The synthesized adsorbent exhibited a high adsorption ability such as a high K_d , uptake and capacity for Pt(II) and Pd(II) in dilute aqueous solutions.

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REFERENCES

Brown, J., Mercier, L. and Pinnavaia, T. J., "Selective Adsorption of Hg^{2+} by Thiol-functionalized Nanoporous Silica," *Chem. Commun.*,

- 69 (1999).
- Chah, S., Kim, J. S. and Yi, J., "Separation of Zinc Ions from Aqueous Solutions using Modified Silica Impregnated with CYANEX 272," *Separation Science and Technology*, **37**, 701 (2002).
- Choi, S.-H. and Nho, Y. C., "Adsorption of Pb^{2+} , Cu^{2+} and Co^{2+} by Polypropylene Fabric and Polyethylene Hollow Fiber Modified by Radiation-Induced Graft Copolymerization," *Korean J. Chem. Eng.*, **16**, 241 (1999).
- Dai, S., Burleigh, M. C., Ju, Y. H., Gao, H. J., Lin, J. S., Pennycook, S. J., Barnes, C. E. and Xue, Z. L., "Hierarchically Imprinted Sorbents for the Separation of Metal Ions," *J. Am. Chem. Soc.*, **122**, 992 (2000).
- Kim, J. S., Chah, S. and Yi, J., "Preparation Modified Silica for Heavy Metal Removal," *Korean J. Chem. Eng.*, **17**, 118 (2000).
- Lee, B., Kim, Y., Lee, H. and Yi, J., "Synthesis of Functionalized Porous Silicas via Templating Method as Heavy metal Ion Adsorbents: The Introduction of Surface Hydrophilicity on the Surface of Adsorbents," *Microporous and Mesoporous Materials*, **50**, 77 (2001).
- Liu, J., Feng, X., Fryxell, G. E., Wang, L.-Q., Kim, A. Y. and Gong, M., "Hybrid Mesoporous Materials with Functionalized Monolayers," *Adv. Mater.*, **10**, 161 (1998).
- Liu, R., Li, Y. and Tang, H., "Synthesis and Characteristics of Chelating Fibers Containing Imidazoline Group or Thioamide Group," *Journal of Applied Polymer Science*, **83**, 1608 (2002).
- Socrates, G., "Infrared Characteristic Group Frequencies," John Wiley & Sons (1994).
- Stein, A., Melde, B. J. and Schroden, R. C., "Hybrid in Organic-Organic Mesoporous Silicate-Nanoscale Reactors Coming of Age," *Adv. Mater.*, **12**, 1403 (2000).
- Talanova, G. G., Zhong, L., Kravchenko, O. V., Yatsimirskii, K. B. and Bartsch, R. A., "Noble Metal Ion Sorption by Pyridyl and Bipyridyl Group-containing Chelating Polymers," *Journal of Applied Polymer Science*, **80**, 207 (2001).