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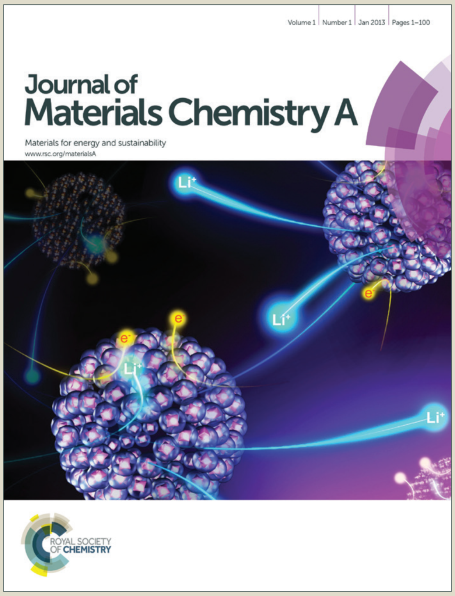

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ARTICLE

Chemically stable magnetic nanoparticles for metal adsorption and solid acid catalysis in aqueous media

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We have developed a magnetically collectable, reusable adsorbent and catalyst for concentrating heavy metal ions in acidic aqueous solutions and solid acid catalysis in aqueous media. Chemically stable, magnetic rattle-type core-shell particles, comprising metallic cobalt nanoparticles in hollow silica microspheres, were prepared by the sol-gel reaction of alkylsilyl trichlorides around water droplets in a water-in-oil emulsion. Sulfonic groups were immobilized on the external surface of the core-shell particles through silylation with 3-mercaptopropyl(trimethoxysilane) and subsequent oxidization of the thiol groups by nitric acid. The sulfonic groups acted as adsorption sites for Zn and Pb ions under acidic conditions and as catalytically active sites for the hydrolysis of ethyl acetate in aqueous media. The enclosed Co was not eroded during the regeneration of the adsorbent/catalyst by 1 M HCl. The chemical stability arose from the dense non-porous shell, which prevents the passage of solvents.

Introduction

The functionalization of magnetic nanoparticles by hybridization has received much attention in many areas, such as industrial chemistry and biomedical engineering, for separation, transportation, and imaging by external magnetic fields.[1-6] Agents that are environmentally compatible with water and biological systems, and agents that respond to stimuli such as heat[7,8] and light[9], have been used for functionalization. Ultrafine particles and fibers have recently been developed as adsorbents for the remediation of toxic metals from wastewater.[10-13] Active sites for adsorption and catalysis have also been immobilized on magnetic nanoparticles to create adsorbents and catalysts that are magnetically separable from liquid media. This prevents clogging during filtration and recovery that is more energetically efficient and faster than centrifugation. Superparamagnetic properties are important for magnetic separation because they allow easy recovery and dispersion in response to external magnetic fields.[14] It is necessary to prevent the nanoparticles agglomerating in order to maintain their nanomagnetic functionality. Thus, core-shell, or A@B particles (A: core, B: shell), have been prepared using various synthetic strategies, including self-assembled monolayers, layer-by-layer deposition, and sol-gel reactions.[6,15-17]

Chemically stable magnetism, where the magnetic particles are protected from oxidation and dissolution, is a prerequisite for reusable adsorbents, catalysts, and biomedical agents. Therefore, the stability of the nanoparticles has been investigated in various atmospheres and liquids.[18-27] There are several examples of magnetic nanoparticles in aqueous solutions.[27-46] For example in A@B particles, A components of magnetite (Fe_3O_4),[27-38] and maghemite (γ-Fe_2O_3),[39-45] FePt,[46] and B components of organic polymers,[31-33,42] amines,[34] acids,[35,36,43] cyclodextrins,[46] silica (organosilicas),[27-30,38-40] titania[41] and titanosilicates[44] have been reported. Using modified magnetic nanoparticles for heavy metal adsorption[30,32,33,35,36,38,39,42,43] is problematic under acidic conditions, because methods for modification are limited. Silica is a useful shell substance, owing to its acid-tolerance[26] as well as its varied structural and morphological forms. A dense silica shell, which prevents the passage of water, is necessary to protect the core magnetic compound. The thickness and density of the silica shell can be controlled by varying the amount of silica precursors and by tuning the polycondensation, respectively, to provide chemically stable magnetic nanoparticles.

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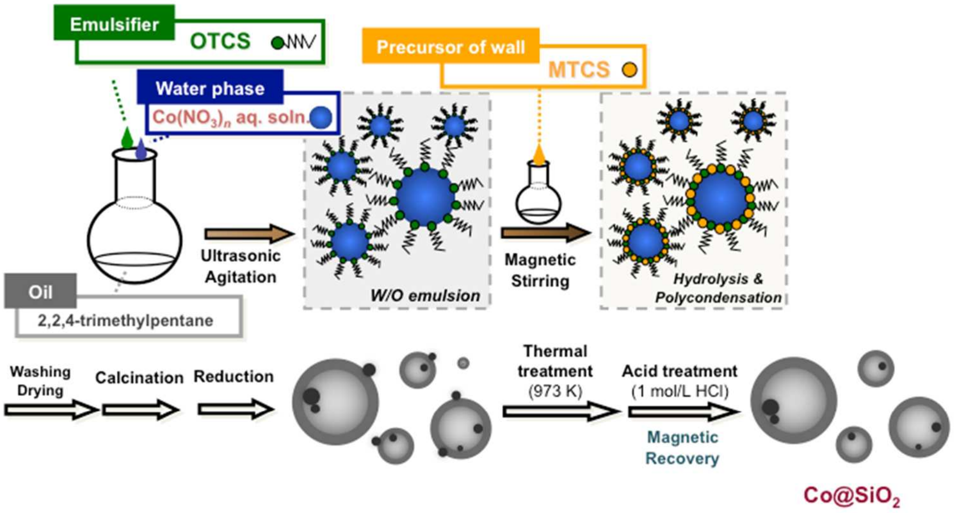

Scheme I. Schematic drawing of the preparation of $Co@SiO_2$ particles.

We have developed magnetically collectable and reusable functional particles for heavy-metal ion-concentration in acidic solution and solid acid catalysis in aqueous media. For this purpose, sulfonic groups, which are allowed to act as repeated cation exchange and acid-catalyzed reactions, were anchored covalently on the external surface of magnetic rattle-type Co@silica core-shell particles with a dense silica shell. The synthetic approach of the magnetic core-shell particles was based on the deposition of a polyalkylsiloxane shell, which is the precursor of the silica shell, on water droplets in a water-in-oil (W/O) emulsion through the sol-gel reaction of octyl- and methyl-trichlorosilanes.[47,48] The water droplets contained the cobalt nitrate starting material for the magnetic particles. The vaporization of the water in the resulting capsules, followed by calcination, reduction and annealing, resulted in metallic cobalt particles enclosed by a dense silica shell (Scheme I).[49,50] Because of the dense silica shell, the covalently attached sulfonic groups on the magnetic particles were successfully regenerated by 1 M HCl after they had adsorbed heavy metals (Zn(II) and Pb(II)) without eroding the enclosed Co particles. Moreover, the sulfonic groups acted as a catalytically active site in water for hydrolysis of ethyl acetate.

Experimental

Chemicals and Reagents.

Octyltrichlorosilane (OTCS) and methyltrichlorosilane (MTCS) were purchased from Aldrich Chemical Co., Ltd., and Shin-Etsu Chemical Co., Ltd., respectively. Cobalt(II) nitrate hexahydrates, isooctane (2,2,4-trimethylpentane), hexadecyltrimethylammonium bromide, 3-mercaptopropyl(trimethoxysilane) (MPS), and dry toluene were purchased from Wako Chemical Co., Ltd. These materials were used as received.

Preparation of Rattle-type Co Particles Encapsulated in a Dense Silica Shell (Scheme I).

Rattle-type Co core and silica shell particles ($Co@SiO_2$) were prepared by using a previously reported procedure.[50] A W/O emulsion was created by mixing water (0.22 mL), an aqueous solution of $Co(NO_3)_2$ (0.75 mL, 3.0 mol kg^{-1}), and OTCS (2.97 g) in isooctane (50 mL) by ultrasonic agitation. After 5 min ultrasonic irradiation (45 kHz, 100 W), the mixture was allowed to stand for 5 min at room temperature. The ultrasonic agitation was repeated three times. MTCS (1.34 g) in isooctane (10 mL) was poured into the W/O emulsion under magnetic stirring. The mixture was stirred at room temperature for more than 3 h to form polymethylsiloxane shells around aqueous droplets. During the reaction, air saturated with water vapor (0.1 L min^{-1}) was continuously supplied. After filtration, the product was washed with isooctane and then dried at 323 K for 1 day.

The dried product was heated at 393 K in air for 1 day, and then calcined at 873 K in an electronic furnace for 3 h. The calcined solid was treated under a flow of H_2 (5 mL min^{-1}) at 773 K for 3 h, and subsequently heated at 973 K for 3 h in a flow of N_2 (10 mL min^{-1}). The product was then washed with 1 M HCl. The acid-treated sample was recovered using neodymium magnets.† The recovered sample was thoroughly washed with water before further magnetic recovery to obtain $Co@SiO_2$ particles. The amount of Co in the $Co@SiO_2$ particles was estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis after it was converted to aqueous form by alkali fusion. The amount of the Co leached during immersion of $Co@SiO_2$ (20 mg) in an aqueous solution of 1 M HCl (4 mL) for 7 days was also determined by ICP-AES. Before the experiment, the sample was dried at 323 K overnight.

Immobilization of Sulfonic Groups on $Co@SiO_2$.

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Reactions of MPS with Co@SiO_2 were carried out using a procedure based on the silylation of a layered alkali silicate.[51] Before the silylation, Co@SiO_2 (0.52 g) was immersed in an aqueous 1 M NaOH solution (200 mL) for 12 h at room temperature. The alkali-treated particles were dispersed in a solution of hexadecyltrimethylammonium bromide (1.3 g) in water/ethanol (1:1 v/v). The resulting solid was transferred into a solution of MPS (0.4 mL) in dry toluene (80 mL). The mixture was heated for 3 h at 333 K and then concentrated under reduced pressure at 333 K for 2 h to evaporate the toluene. The product was washed with a mixture of 0.1 M HCl aqueous solution and ethanol (1:1 v/v). The washed solid was allowed to react with aqueous 7 M HNO_3 (50 mL) for 6 h. After washing with water, the solid product was magnetically collected,† and the supernatant was decanted. The product was dried at 323 K in air.

The cation exchange capacity was determined by the reaction of NaCl with the protons of the trisilylpropylsulfonic groups. The sample was allowed to react with an aqueous 4 mass % NaCl solution, and then the resulting solid was recovered with a magnet.† These steps were repeated to complete the exchange reactions. The supernatant was titrated with NaOH aqueous solution.

Adsorption of Transition Metal Ions.

The sample modified with sulfonic groups (0.08 g) was allowed to react with aqueous solutions containing transition metal ions (20 mL, $ZnCl_2$ or $Pb(NO_3)_2$, initial pH of 2.5 or 5.2) in a Pyrex flask for 24 h at 298 K with reciprocal shaking. After the reactions, the adsorbent was recovered magnetically.† The initial concentrations of $ZnCl_2$ or $Pb(NO_3)_2$ were 0.4 and 4 mM, which correspond to the cation exchange capacity and to 10-fold the cation exchange capacity, respectively. Blank samples containing the aqueous solutions (20 mL), without adsorbents, were also prepared to estimate the adsorption of the metal ions to the Pyrex flask. The amount of metal ions adsorbed on the sample was determined by ICP-AES analysis from the difference between the concentration of the metal ions in the supernatant and that of the blank sample. In order to verify the regeneration of the adsorbent, sample was immersed in 1 M HCl aqueous solution with reciprocal shaking for 6 h, followed by the above recycling adsorption experiment. The amount of Co ions leached during the adsorption and the regeneration was estimated by ICP-AES.

Hydrolysis of Ethyl Acetate in Aqueous Solution.

Hydrolysis of ethyl acetate was conducted in a 2-necked Pyrex flask equipped with a refluxing condenser and thermometer. The reaction of the sample modified with sulfonic groups (0.1 g) was carried out at 343 K for 2 h with stirring using an aqueous solution of ethyl acetate (30 mL, 18 mmol ethyl acetate). The amount of catalyst used in the first run was 2.0×10^{-5} mmol. After the first run, the recycling reaction was performed. After the first run, the resulting aqueous suspension was transferred to a glass vial, and the catalyst was recovered magnetically† before the reaction mixture was decanted. The catalyst after the reaction was washed with aqueous 4 mass % NaCl solution to estimate the cation exchange capacity. After washing with aqueous 1 M HCl, the catalyst was immersed in a fresh ethyl acetate solution to perform the recycle reactions as described above. The reactant and products (ethanol and acetic acid) were commercial guaranteed reagents (Wako Pure Chemicals) and were used as received. All the solutions were prepared from Elix-UV pure water (Millipore). The products were analyzed with a gas chromatograph using a DB-WAX capillary column (Agilent J&W).

Instruments.

X-Ray powder diffraction (XRD) patterns were obtained by using Rigaku RINT 2200V/PC diffractometer (monochromatic Cu Kα radiation), operated at 20 mA and 40 kV. Fourier transform-infrared (FT-IR) spectra were recorded on a JASCO FT/IR-4200 spectrophotometer using the KBr pellet method. Scanning electron micrographs were obtained on a Hitachi S-4100 field-emission scanning electron microscope (SEM) at an accelerating voltage of 15 k. The transmission electron micrographs with energy dispersive X-ray (EDX) mapping were obtained on a Hitachi High-Tech HD-2300A spherical aberration corrected scanning transmission electron microscope (STEM) equipped with an EDAX Genesis XM 4 EDX spectrometer (accelerating voltage of 200 kV). Nitrogen adsorption-desorption isotherms at 77 K were obtained by using a BEL Japan BELSORP-mini instrument. Before the adsorption experiments, the samples were heat-treated at 473 K under reduced pressure. ICP-AES was performed on Hitachi-HighTech SPS5510 spectrometer. Magnetization curves were obtained from a Toei Kogyo VSM-5S vibrating sample magnetometer (VSM). X-ray photoelectron spectroscopy (XPS) was performed on a JEOL JPS-9010MX photoelectron spectrometer (Mg Kα radiation, 1253.6 eV), operated at 20 mA and 10 kV.

Results and Discussion

Preparation of Co@SiO_2.

Ultrasonic agitation of a mixture of OTCS dissolved in an aqueous solution of 2,2,4-trimethylpentane and $Co(NO_3)_2$ formed a blue W/O emulsion. Addition of MTCS produced a light blue precipitate. When the dried precipitate was calcined at 873 K, it turned blue-gray, indicating oxidation to cobalt oxide. The XRD pattern of the calcined sample (Fig. 1a) contains diffraction peaks corresponding to Co_3O_4. The FT-IR absorption bands of the polyalkylsiloxane alkyl groups ($\nu_{C\text{-}H}$ at around 2900 cm^{-1}) and the Si─C bond (at around 1300 cm^{-1}) are weak, indicating calcination turned most of the polyalkylsiloxane to silica (see Electronic Supplementary Information, Fig. S1). The specific surface area derived from the BET-plot of the calcined sample N_2 adsorption isotherm was 40 m^2/g. The calcined sample consisted of spherical hollow particles of microporous silica encapsulating cobalt oxides.

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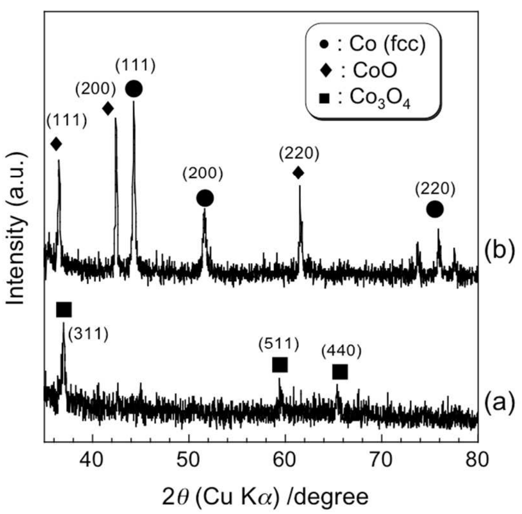

Fig. 1. XRD patterns of (a) precipitate from the W/O emulsion containing $Co(NO_3)_2$ calcined at 873 K and (b) reduced (a) in H_2 gas at 773 K.

Fig. 2a shows the SEM image of particles after they were reduced in H_2 gas then annealed in N_2 at 973 K. Most of the particles were microspheres of various diameters reflected from the variation of the droplet size in the W/O emulsion. The average particle size determined from the SEM observations was 0.26 μm (inset of Fig. 2a). There was no IR absorption band from organic compounds for the annealed sample (Fig. S1c). The specific surface area was decreased by annealing from 40 to 20 m^2/g, suggesting that the silica shell was partly transformed into a dense non-porous phase. In the XRD pattern of the reduced sample (Fig. 1b), CoO and metallic Co (fcc) diffraction peaks were observed, revealing that Co_3O_4 was reduced to metallic cobalt (partially reduced to divalent Co). Hydrogen gas penetrated the porous silica shell during the reduction at 673 K. After heat treatment at 973 K in N_2, the porous silica shell was transformed into dense non-porous silica, although the metallic Co unchanged.

The reduced sample of Co@SiO_2 was agitated in 1 M aqueous HCl and then collected by a magnet. Under our experimental conditions, it took no more than 1 min to gather the particles from the acidic solution. Fig. 2b shows the shape of the Co@SiO_2 was maintained after agitating in 1 M HCl. Although only a slight portion (less than 1%) of larger particles (> 1 μm) was observed, most of the particles are below 1 μm. The average particle size of Co@SiO_2 was 0.25 μm which was similar to that of the reduced sample (0.26 μm), and that the particle size was not altered by the acid treatment (inset of Fig. 2b).

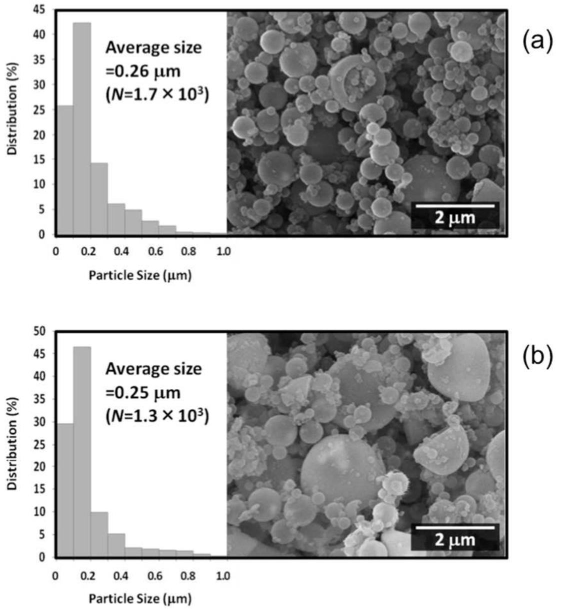

Fig. 2. SEM images of the particles and their particle size distributions (inset). (a) After heating in N_2 at 973 K. (b) After agitating the sample heat-treated at 973 K in 1 M HCl (Co@SiO_2).

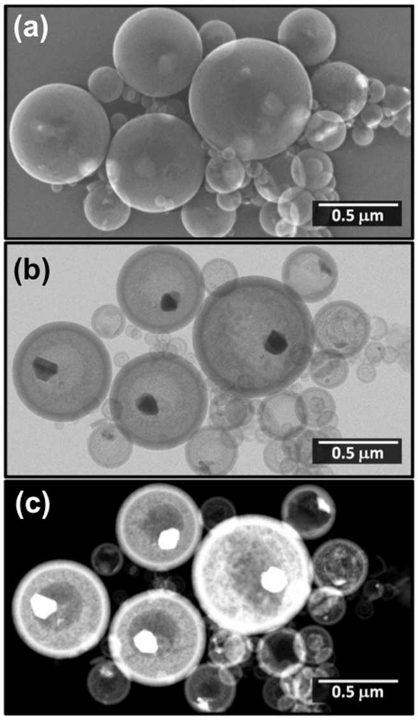

Fig. 3. (a) SEM image, (b) bright-field TEM image, and (c) STEM dark-field image of Co@SiO_2.

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Fig. 3a—c shows SEM, bright-field TEM, and STEM dark-field images of Co@SiO_2. A rattle type core-shell structure was observed in the TEM image for most of the particles. The STEM dark-field image confirmed that the core and shell were composed of cobalt and silica, respectively, because contrast of the core is brighter than that of the shell. The SEM image shows that the Co particles were not present on the silica surface. The majority of the Co agglomerated inside the hollow silica spheres rather than being dispersed as nanoparticles. The amount of Co encapsulated in the Co@SiO_2 particles was 7.8 mass %.

Stability of Encapsulated Magnetic Co Particles under Acidic Conditions.

Fig. 4 shows the response of the Co@SiO_2 particles to a magnet after immersion in 1 M HCl. The particles in the sample bottle were attracted to the magnet, confirming that the Co@SiO_2 nanoparticles were acid-tolerant magnetic particles. The color change of the pH indicator paper from yellow to red in acidic solution is also shown in this figure. The magnetism persisted, even after the nanoparticles were immersed in HCl for 1 year. The VSM results showed that saturation magnetization of 4.0 emu/g[50] did not decrease substantially during 1 week in 1 M HCl aqueous solution, showing that the Co@SiO_2 particles were acid tolerant.

Fig. 4. The behaviour of Co@SiO_2 exposed to a magnet (right-side) after immersion in 1 M HCl. Particles in the sample bottle were attracted to the magnet. The photograph also shows that the color of the pH indicator paper turned from yellow to red in the acid solution.

Because metallic cobalt and magnetite are readily dissolved in mineral acids,[52] the stability tests verified that the magnetic particles can be shielded from acidic solution by the dense silica shell. Aslam et al.[25] fabricated Co@SiO_2 nanoparticles from tetramethylorthosilicate and $CoCl_2$, and found that the Co-core of the particle dissolved completely in 1 M HCl within 12 h. Their results suggest that the acid solution passed through the silica shell and the Co-core was readily dissolved in the aqueous HCl. In our system, the magnetism was lost in 1 M HCl for both samples that were not heat-treated in N_2 at 973 K. In contrast, Co@carbon nanoparticles are stable in HNO_3 (53 wt %) for 2 months[22]. This indicates that the majority of the Co particles was protected by dense shells. Therefore, the acid-tolerant properties of the Co@SiO_2 nanoparticles were attributed to the formation of dense non-porous shell.

Immobilization of Sulfonic Groups on Co@SiO_2.

After the reaction of the alkali-treated Co@SiO_2 with MPS, the propyl group H—C—H bending absorption band appeared around 1400 cm^{-1}, indicating that the MPS silylation of Co@SiO_2 succeeded. The XPS spectrum in Fig. 5 shows that the thiol groups on Co@SiO_2-MPS were oxidized by 7 M aqueous HNO_3; the S2p core-level spectrum indicates that most of the thiol groups (164 eV) were oxidized to sulfonic groups (169 eV),[53] and the oxidized product, Co@SiO_2-SPS, was formed (The XPS survey spectrum is shown in Electronic Supplementary Information, Fig. S2). The amount of sodium ions exchanged with the protons on Co@SiO_2-SPS was 0.20 mmol/g. The amount slightly decreased during the second run of the treatment with NaCl and subsequent aqueous HCl solutions to 0.18 mmol/g. The occupied area of the trisilylpropyl sulfonic acid group was calculated to be 7×10^{-2} nm^{-2} from the specific surface area derived from the N_2 adsorption isotherm for Co@SiO_2 (7 m^2/g) and the cation exchange capacity, indicating MPS polymerization and silylation on Co@SiO_2.

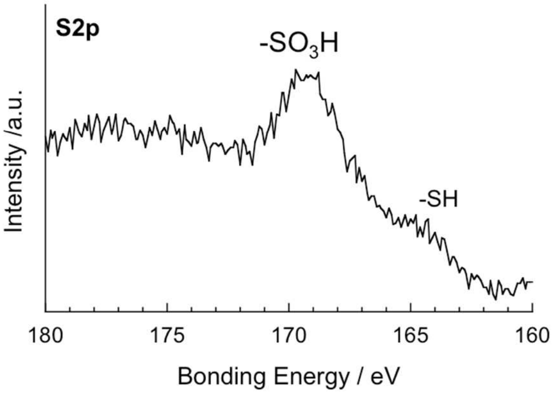

Fig. 5. XPS S2p core-level spectrum of Co@SiO_2-SPS.

An SEM image of the Co@SiO_2-SPS particles is shown in Fig. 6a. They are spherical with an average particle size of 0.7 µm. The TEM (Fig. 6b) and STEM dark-field images (Fig. 6c) together with EDX elemental maps (Si and Co) for a typical Co@SiO_2-SPS particle show a Co core and a silica shell. The amount of Co encapsulated in the Co@SiO_2-SPS particles was determined by ICP to be 6.1 mass %. Although the amount of Co ions lost during silylation and oxidation was about 20% of the total Co in the Co@SiO_2 particles, the magnetism was verified by the fact that the Co@SiO_2-SPS particles in 7 M HNO_3 were attracted to a magnet (Fig. 7). The magnetization at 12 kOe was calculated as 3.3 emu/g from the VSM curves in Fig. 7. The small remanence of Co@SiO_2-SPS nanoparticles is an advantage for their use as magnetically collectable reusable adsorbents and catalysts.

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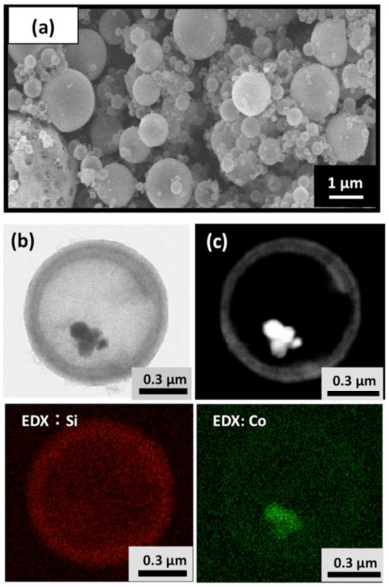

Fig. 6. (a) SEM, (b) TEM, (c) STEM dark-field image of Co@SiO_2-SPS. Elemental mapping images of Si and Co are shown at the bottom.

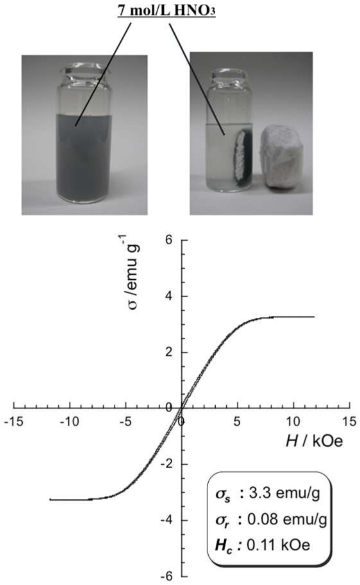

Fig. 7. (Top) Photograph of Co@SiO_2-SPS particles attracted to a magnet after they were immersed in 7 M HNO_3 to oxidize the thiol group. (Bottom) Magnetization curves of Co@SiO_2-SPS measured at room temperature.

Adsorption of Transition Metal Ions.

The results of the adsorption of Zn and Pb ions from aqueous solutions on Co@SiO_2-SPS are summarized in Table 1. At pH 5.2, the amount of zinc ions adsorbed from a lower concentration solution (0.4 mM) was 0.05 mmol/g. As shown in Fig. 8, zinc ions rapidly were adsorbed, and the saturation reached within 24 h under the present experimental condition. The amount of adsorbed lead ions from the solution of the same concentration was 0.04 mmol/g, which was slightly smaller than that of zinc ions. When the solution pH was changed to 2.5, it slightly decreased the amount of metal ions adsorbed. When the amount of zinc(II) chloride was increased to 10-fold the cation exchange capacity, the amount of zinc ions adsorbed increased to 0.08 mmol/g, which is similar to the value of the cation exchange capacity of Co@SiO_2-SPS (0.2 mequiv/g), irrespective of the solution pH. Thus, the adsorption behavior of the transition metal ions for the sulfonic groups on the Co@SiO_2-SPS particles can be explained by surface charge and proton competition. We consider that the majority of the incorporated divalent cations are occupying two exchange sites as reported in a sulfonic acid functionalized silica system.[54] For comparison, the adsorption capacity of some adsorbents (layered silicates,[55,56] an activated carbon,[57] a cellulose fiber,[11] and magnetic particles[36,38]) for Zn(II) and Pb(II) is listed in Table 2. During the adsorption experiments, the amount of Co leached from the adsorbent was negligible and was less than 1% of the total Co in the Co@SiO_2-SPS (less than 5×10^{-4} mmol in 20 mL of solution).

A transparent supernatant was obtained after the resulting suspension was transferred into a glass bottle with neodymium magnets† for 3 min. The Co@SiO_2-SPS samples with adsorbed metal ions were regenerated by immersion in 1 M aqueous HCl with reciprocal shaking. There was no substantial decrease in the amount of metal ions adsorbed on the regenerated Co@SiO_2-SPS after the third run, showing that the adsorption was reversible. We also confirmed that the cation-exchange capacity determined by the reaction with NaCl was maintained after the third run to be 0.17 meq/g. Time to require the regeneration by immersing in 1 M HCl was within 2 h. During immersing in HCl for 6 h, less than 1% of the total Co in the Co@SiO_2-SPS particles was eluted during the regeneration process (Table 1). Acidic regeneration has been examined in an EDTA/chitosan modified magnetic Fe_3O_4-silica system.[38] Because of covalently attached sulfonic groups in our system, it is allowed to regenerate the sorption sites by an acidic solution without degradation. Thus, the Co@SiO_2-SPS nanoparticles are suitable as a magnetically collectable and reusable adsorbent for transition metal ions in water.

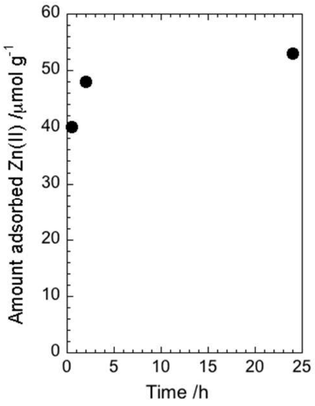

Fig. 8. Time course of adsorption of zinc ions on Co@SiO_2-SPS (initial concentration of 0.4 mM).

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Table 1. Summary of the results of the adsorption and regeneration cycles for Co@SiO_2-SPS.

Run	Amount of metal ions added (× cation exchange capacity of Co@SiO_2-SPS)	Adsorption of zinc ions						Adsorption of lead ions					
		pH 2.5			pH 5.2			pH 2.5			pH 5.2		
		Adsorbed metal ions ($\mu mol \cdot g^{-1}$)	Co-leaching (%)[1]		Adsorbed metal ions ($\mu mol \cdot g^{-1}$)	Co-leaching (%)[1]		Adsorbed metal ions ($\mu mol \cdot g^{-1}$)	Co-leaching (%)[1]		Adsorbed metal ions ($\mu mol \cdot g^{-1}$)	Co-leaching (%)[1]	
			During adsorption	During regeneration		During adsorption	During regeneration		During adsorption	During regeneration		During adsorption	During regeneration
1	1	45	1.4	1.0	53	0.5	0.6	36	0.5	0.3	41	0.4	0.3
	10	83	0.2	0.2	82	0.2	0.3	-	-	-	-	-	-
2	1	40	0.3	0.4	51	0.3	0.4	34	0.3	0.2	41	0.3	0.2
	10	77	0.2	0.3	80	0.2	0.3	-	-	-	-	-	-
3	1	43	0.4	0.4	53	0.4	0.4	31	0.3	0.3	38	0.3	0.3
	10	-	0.2	0.3	86	0.2	0.3	-	-	-	-	-	-

1: The denominator is the total amount of Co in Co@SiO_2-SPS (6 mass %).

Table 2. Adsorption capacity of layered silicates, an activated carbon, a cellulose fiber, and magnetic particles for zinc and lead ions.

Adsorbent	Metal ion	Adsorption capacity meq/g	ref
Fe_3O_4@EDTA modified organosilica	Pb(II)	0.4	38
Water soluble Fe_3O_4	Pb(II)	1.0	36
Cellulose fiber	Pb(II)	0.1	11
Activated carbon	Pb(II)	0.2	57
Na-4-mica	Zn(II)	3.0	56
Montmorillonite	Zn(II)	0.4	55
Magadiite	Zn(II)	1.0	55
Co@SiO_2-SPS (present study)	Zn(II), Pb(II)	0.2	-

Hydrolysis of Ethyl Acetate in Aqueous Solution.

Table 3 lists the catalytic activity of Co@SiO_2-SPS for the hydrolysis of ethyl acetate. The activity was estimated from the amount of acetic acid produced after 2 h, and was normalized by time and the amount of immobilized sulfonic groups. The activity per unit acid site was comparable to values reported for H_2SO_4 and other solid acids (e.g. H-ZSM-5, Nafion, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$).[58-60] The reactions became stable after a second run, suggesting that Co@SiO_2-SPS nanoparticles can be reused without any significant loss of activity. The negligible difference in the cation exchange capacity of Co@SiO_2-SPS suggests that the active catalytic active sites were not degraded by repeated reactions, and that there was no significant erosion of Co from the catalyst support which poisoned the active sites. Ether hydrolysis[27] and Mannich reactions[40] in water over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mounted amine-modified silica containing magnetic iron oxides have been reported, and resulted in negligible leaching of the iron[27] and the cesium acidic salt[39]. Gill et al.[61] and Takagaki et al.[62] reported acid-catalytic reactions over $CoFe_2O_4$@sulfonic acid-modified organosilica core-shell particles in organic solvents and in water, respectively. Co@SiO_2-SPS nanoparticles are the first example of a magnetically collectable reusable solid acid, with cation exchange ability, which does not undergo substantial erosion of the magnetic particles.

Table 3. Summary of the results of the hydrolysis of ethyl acetate over Co@SiO_2-SPS.

Runs	Hydrolysis of ethyl acetate		
	Conversion (%)	Rate per unit of acid (10^2 mmol·(acid-mol)$^{-1}$·min^{-1})	Cation exchange capacity (mmol·g^{-1})
1	1.0	0.8	0.19
2	2.0	2.2	0.16
3	1.8	2.1	0.18

Conclusions

We have successfully produced chemically stable magnetic particles which remove Zn(II) and Pb(II) ions and function as a solid acid catalyst in water. Rattle-type Co@SiO_2 particles were prepared and trisilylpropyl sulfonic acid was grafted to the silica surface. Because of the dense silica shell, the adsorbent could be regenerated without losing the magnetism, even after treatment with 1 M HCl. The catalytic activity for the hydrolysis of ethyl acetate in water was not decreased substantially, even after activation by 1 M HCl. In addition, the multi-functional magnetic particles were readily recovered with neodymium magnets. The reusability and the retention of magnetism are important for the practical use of magnetically collectable adsorbents for heavy-metal ions and catalysts.

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† Magnetic recovery in our study has been performed as follows; Neodymium magnets, whose surface magnetic field is 3.8 kOe, located at both sides of a glass bottle (outer diameter of 21 mm). The magnetic field gradient from center of the glass bottle to the magnet was 1.9×10^{2} kOe·m^{-1}.

Electronic Supplementary Information (ESI) available: FT-IR spectra of the dried precipitate from the W/O emulsion containing $Co(NO_3)_2$, the calcination precipitate and that after annealing at 973 K in nitrogen, XPS survey spectrum of Co@SiO_2-SPS. See DOI: 10.1039/b000000x/

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