Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Synthesis of hollow and rattle-type mesoporous silica spheres by treating layered mesoporous silica with a basic solution, and using the spheres as microreactors for two-phase reactions

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Supplementary Information

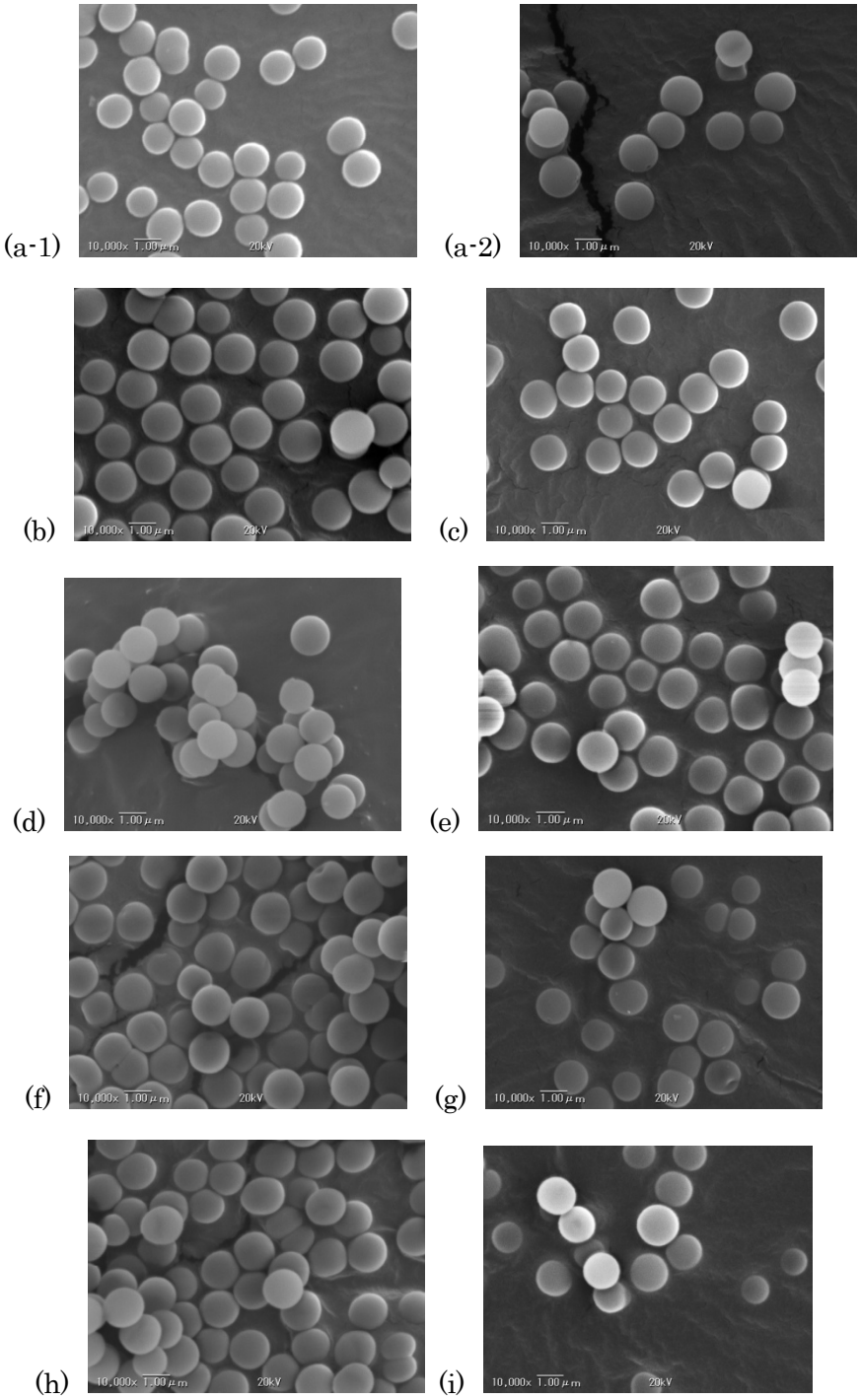

Figure S1 SEM images of mesoporous silica spheres with core-shell structure treated with an ammonia solution in the presence of various surfactants at 25 °C. (a-1) Core , (a-2) core-shell structured spheres before treatment, (b) no surfactant, (c) 6.25×10^{-5} M C_{16}TMACl, (d) 1.25×10^{-4} M C_{16}TMACl, (e) 2.50×10^{-4} M C_{16}TMACl, (f) 1.25×10^{-4} M C_{12}TMACl, g) 1.25×10^{-4} M C_{18}TMACl, (h) 1.25×10^{-4} M sodium hexadecylsulfonate, (i) 1.25×10^{-4} M NH_4Cl.

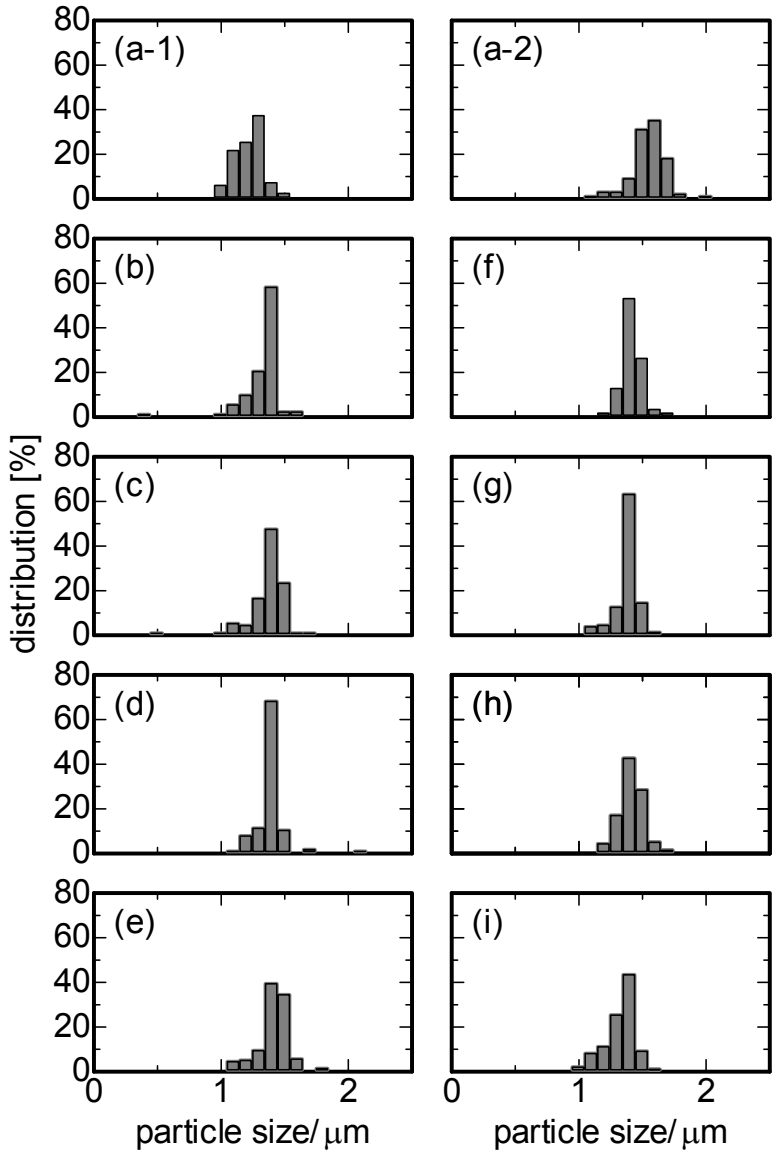

Figure S2 Particle size distributions of mesoporous silica spheres with core-shell structure treated with an ammonia solution in the presence of various surfactants at 25 °C. (a-1) Core , (a-2) core-shell structured spheres before treatment, (b) no surfactant, (c) 6.25×10^{-5} M C_{16}TMACl, (d) 1.25×10^{-4} M C_{16}TMACl, (e) 2.50×10^{-4} M C_{16}TMACl, (f) 1.25×10^{-4} M C_{12}TMACl, g) 1.25×10^{-4} M C_{18}TMACl, (h) 1.25×10^{-4} M sodium hexadecylsulfonate, (i) 1.25×10^{-4} M NH_4Cl.

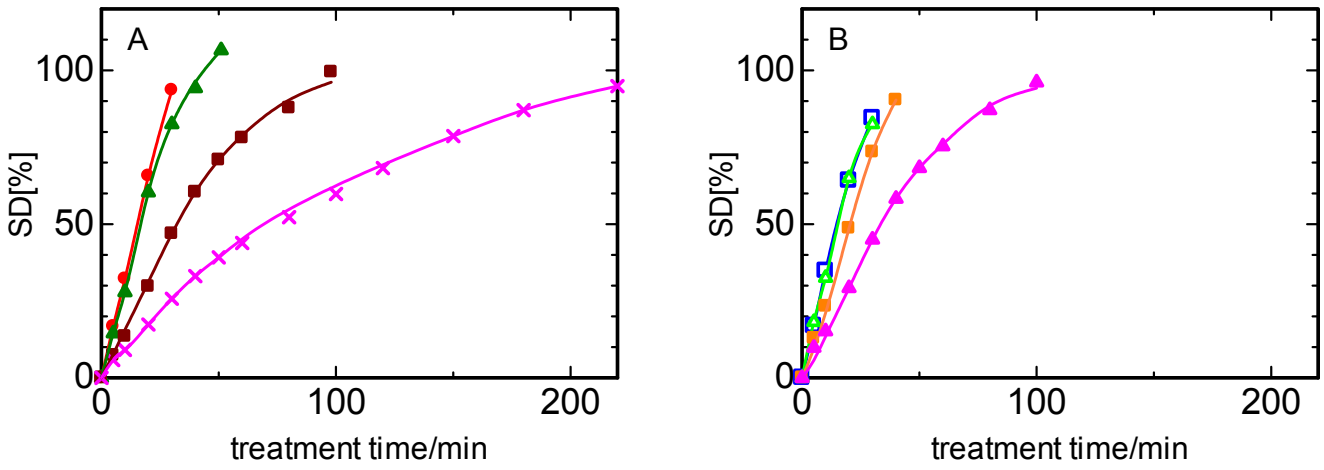

Figure S3 Time courses of silica dissolution of mesoporous silica spheres with core-shell structure in an ammonia solution in the presence of various surfactants at 25 °C. (A) Solid circle: no surfactant, solid triangle: 6.25×10^{-5} M C_{16}TMACl, solid square: 1.25×10^{-4} M C_{16}TMACl, cross: 2.50×10^{-4} M C_{16}TMACl, (B) Amount of additives was 1.25×10^{-4} M. Solid square: C_{12}TMACl, solid triangle: C_{18}TMACl, open square: NH_4Cl, open triangle: sodium hexadecylsulfonate.

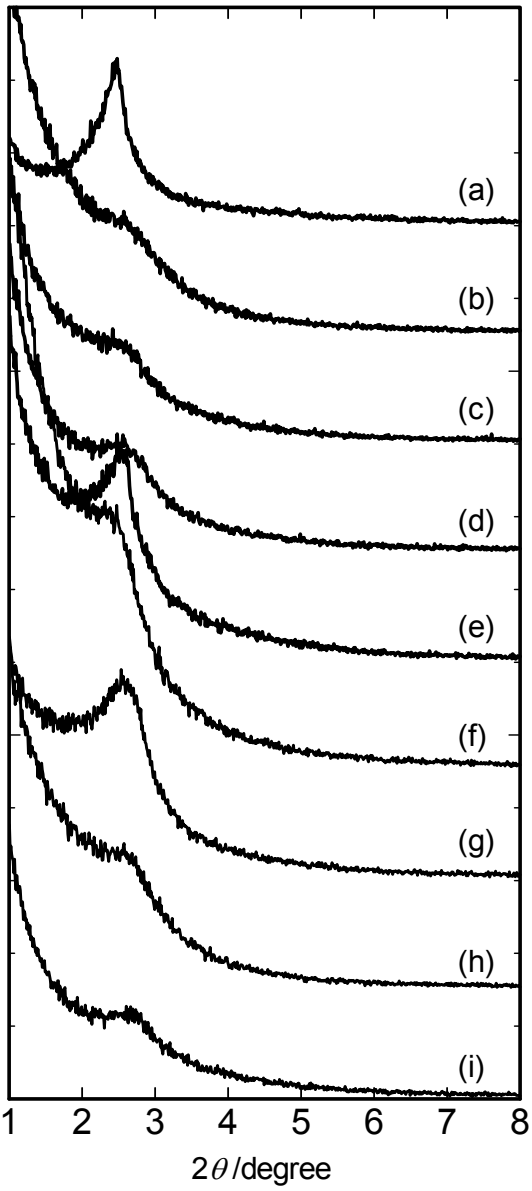

Fig. S4 X-ray diffraction patterns of mesoporous silica spheres with core-shell structure treated with an ammonia solution in the presence of various surfactants at 25 °C. (a) Before treatment, (b) no surfactant, (c) 6.25×10^{-5} M C_{16}TMACl, (d) 1.25×10^{-4} M C_{16}TMACl, (e) 2.50×10^{-4} M C_{16}TMACl, (f) 1.25×10^{-4} M C_{12}TMACl, (g) 1.25×10^{-4} M C_{18}TMACl, (h) 1.25×10^{-4} M sodium hexadecylsulfonate, (i) 1.25×10^{-4} M NH_4Cl.

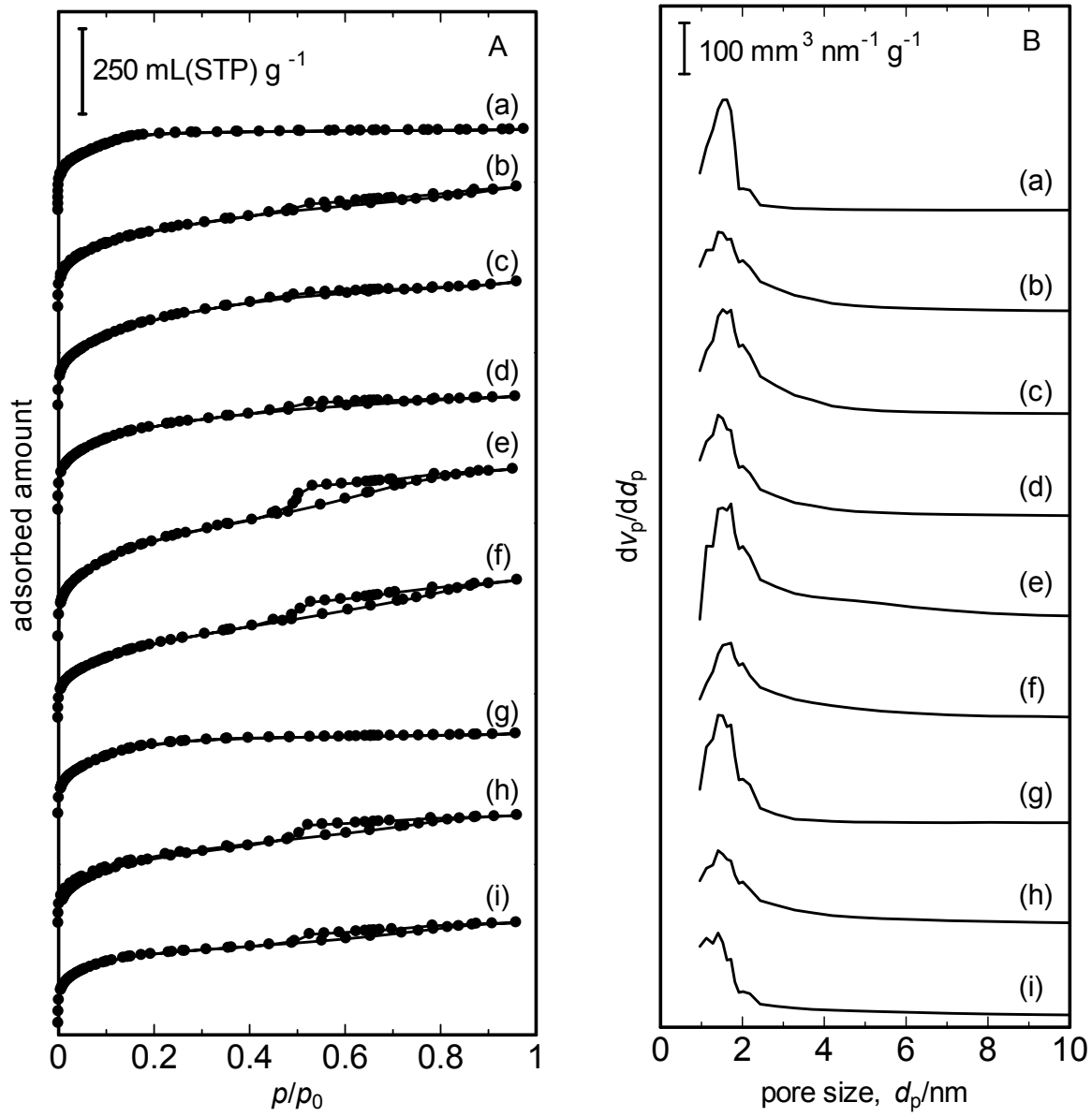

Fig. S5 Nitrogen adsorption-desorption isotherms (A) and pore size distributions (B) of mesoporous silica spheres with core-shell structure treated with an ammonia aqueous solution in the presence of various surfactants at 25 °C. (a) Before treatment, (b) no surfactant, (c) 6.25×10^{-5} M C_{16}TMACl, (d) 1.25×10^{-4} M C_{16}TMACl, (e) 2.50×10^{-4} M C_{16}TMACl, (f) 1.25×10^{-4} M C_{12}TMACl, (g) 1.25×10^{-4} M C_{18}TMACl, (h) 1.25×10^{-4} M sodium hexadecylsulfonate, (i) 1.25×10^{-4} M NH_4Cl.

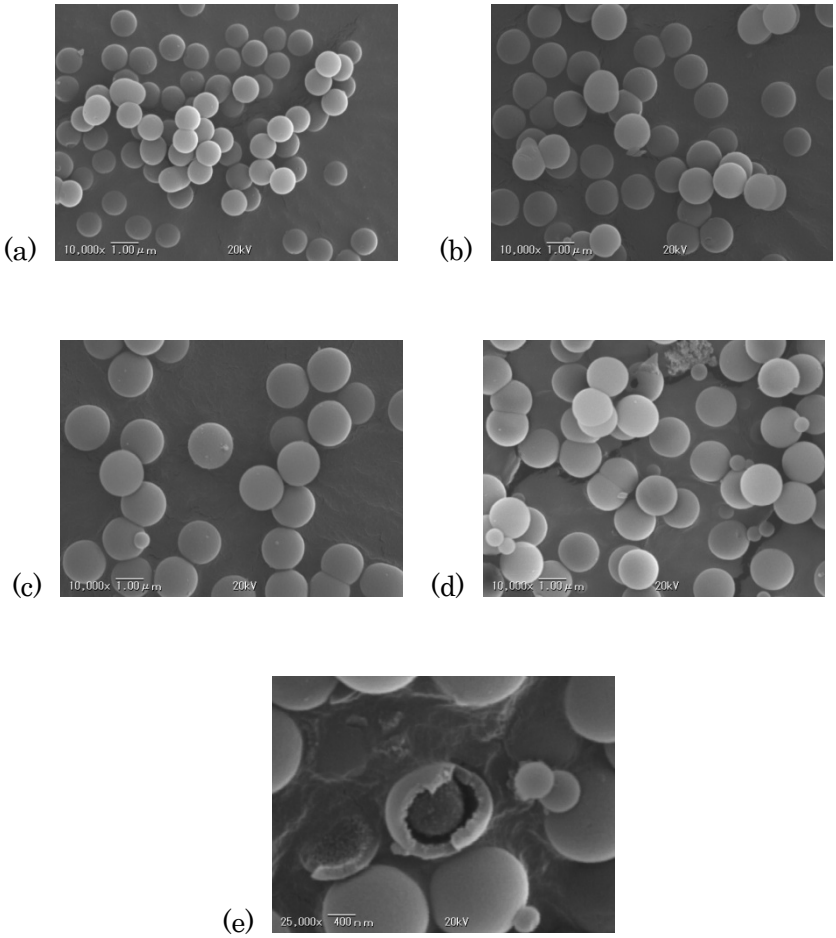

Figure S6 SEM images of mesoporous silica spheres with three layered structure and the spheres treated with an ammonia solution in the presence of 1.25×10^{-4} M C_{18}TMACl at 25 °C. (a) propyl group-grafted mesoporous silica spheres, (b) (a) coated with mesoporous silica, (c) (b) coated with propyl group-grafted mesoporous silica, (d) (c) treated with a basic solution in the presence of 1.25×10^{-4} M C_{18}TMACl, (e) (d) physically broken by a hammer.

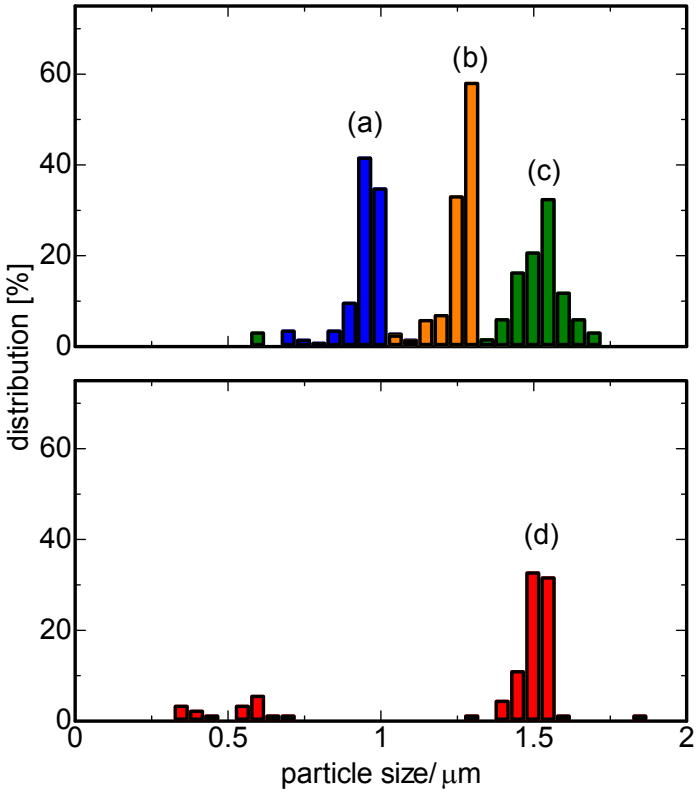

Figure S7 Particle size distributions of mesoporous silica spheres with three layered structure and the spheres treated with an ammonia solution in the presence of 1.25×10^{-4} M C_{18}TMACl at 25 °C. (a) propyl group-grafted mesoporous silica spheres, (b) (a) coated with mesoporous silica, (c) (b) coated with propyl group-grafted mesoporous silica, (d) (c) treated with a basic solution in the presence of 1.25×10^{-4} M C_{16}TMACl.

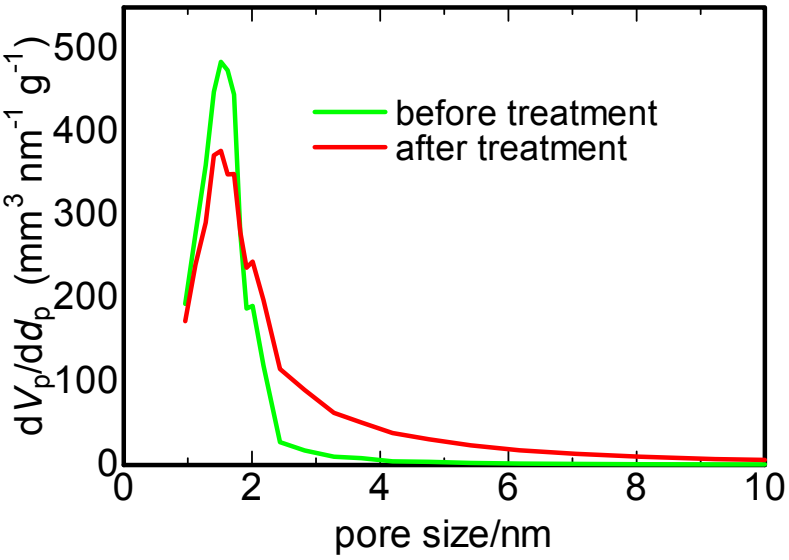

Figure S8 Pore size distributions of mesoporous silica spheres with three layered structure and the spheres treated with an ammonia solution in the presence of 1.25×10^{-4} M C_{18}TMACl at 25 °C.

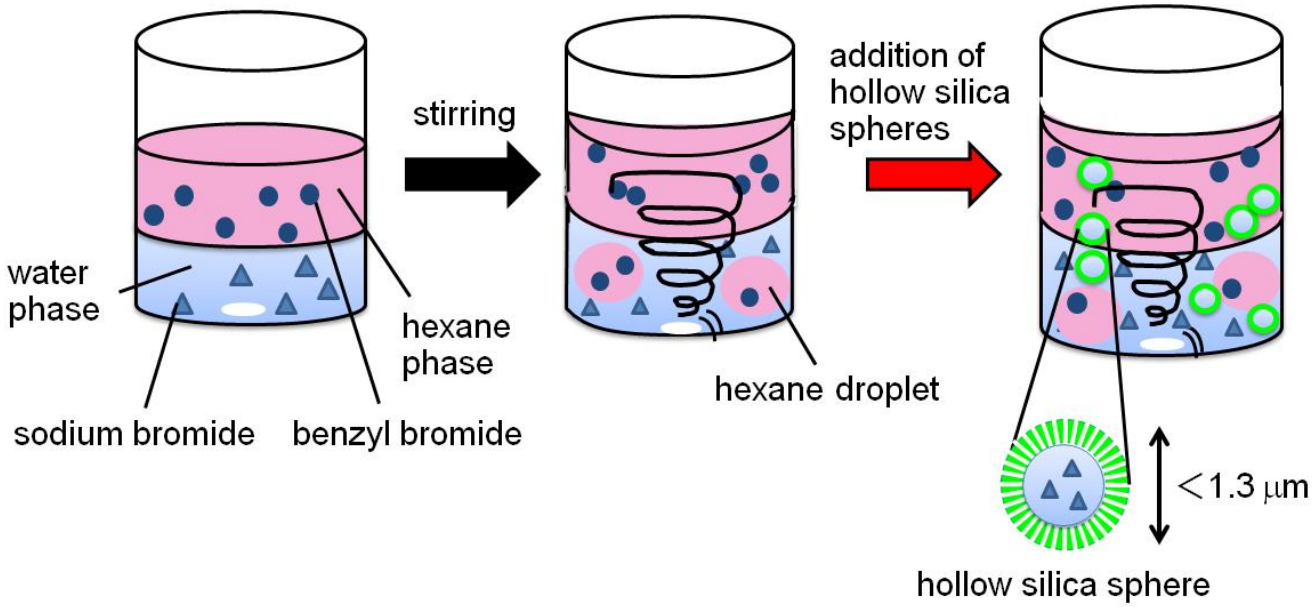

Figure S9 Speculated reaction system in the reaction of benzyl chloride with sodium bromide in the presence of hollow mesoporous silica spheres

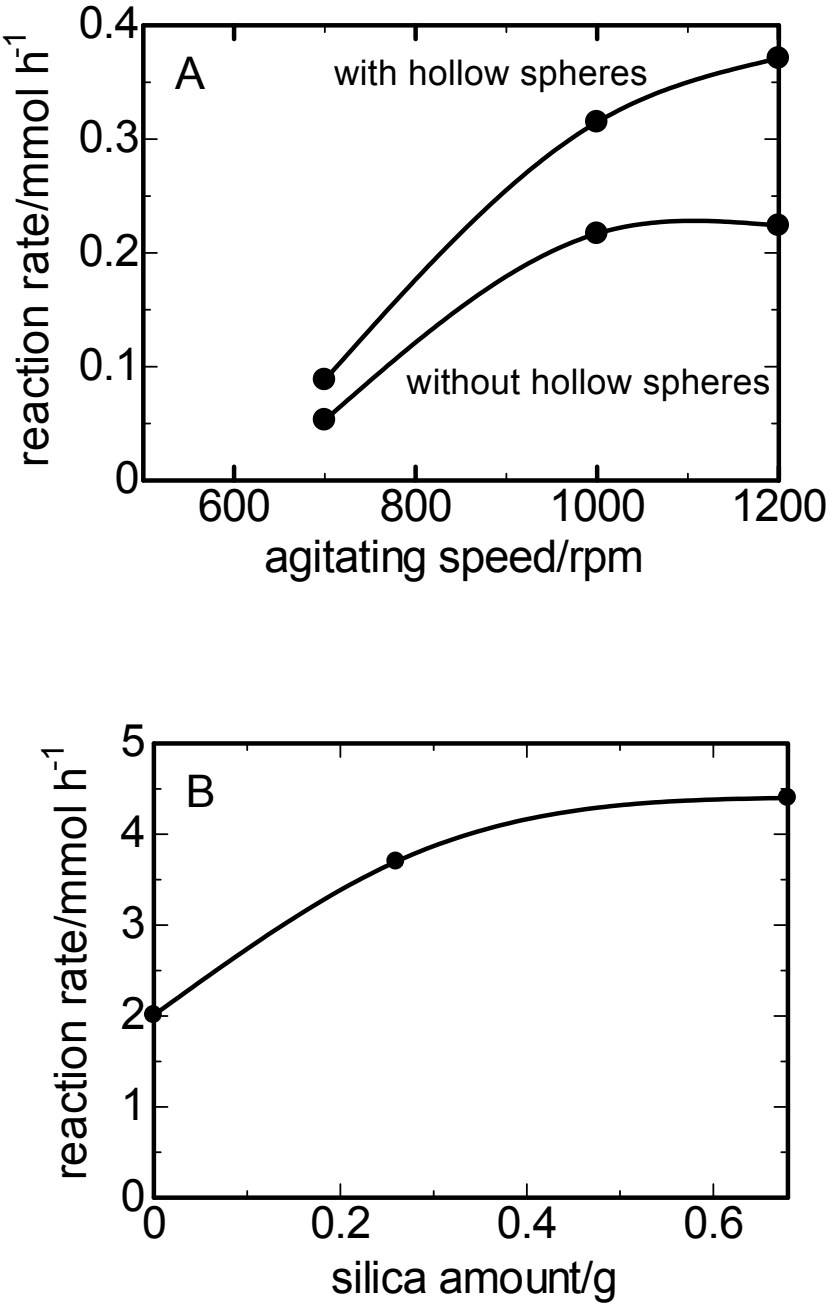

Figure S10 Effects of (A) agitating speed and amount of (B) hollow mesoporous silica spheres on the reaction rate in halogen exchange reaction of benzyl chloride with sodium bromide in the presence of hollow mesoporous spheres. The reaction of 15 mmol of sodium bromide in 2 mL of water and 15 mmol of benzyl chloride in hexane were performed at 100 °C of oil bath temperature. (A) 0.26g of hollow mesoporous silica spheres, (B) 1200 rpm stirring.

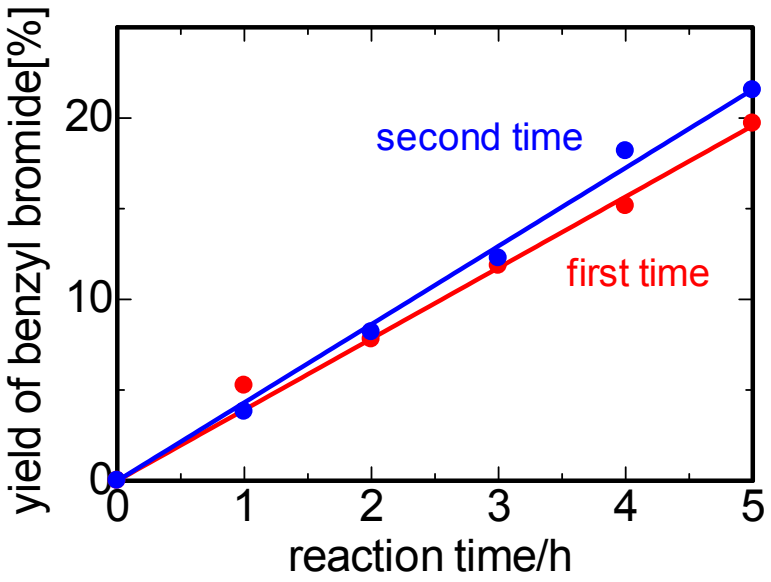

Figure S11 Reuse of the hollow spheres modified with propyl group for the halogen exchange reaction. The reaction of 15 mmol of sodium bromide in 2 mL of water and 15 mmol of benzyl chloride in hexane were performed at 100 °C of oil bath temperature with 1200 rpm stirring in the presence of 0.26 g of the spheres.

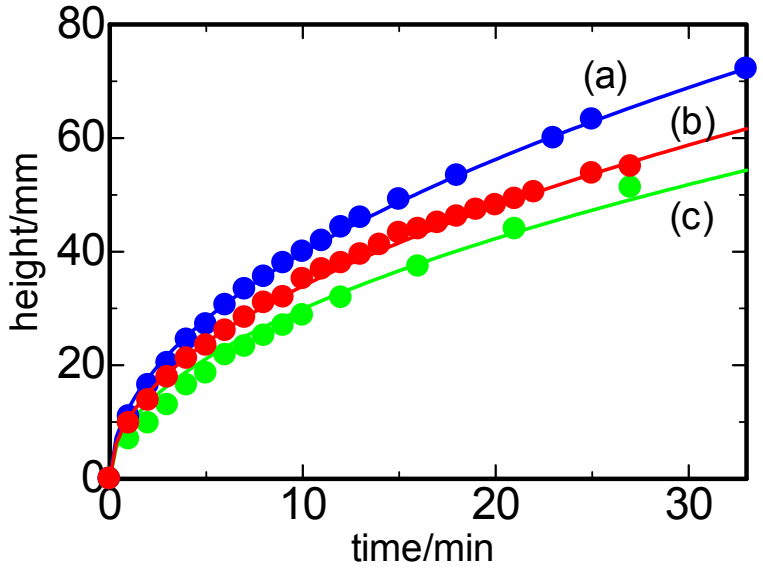

Figure S12 Change in liquid level of hexane in the tubing with modified hollow mesoporous silica spheres with time. (a) Spheres modified with phenyl groups, (b) propyl groups, and (c) methyl groups.

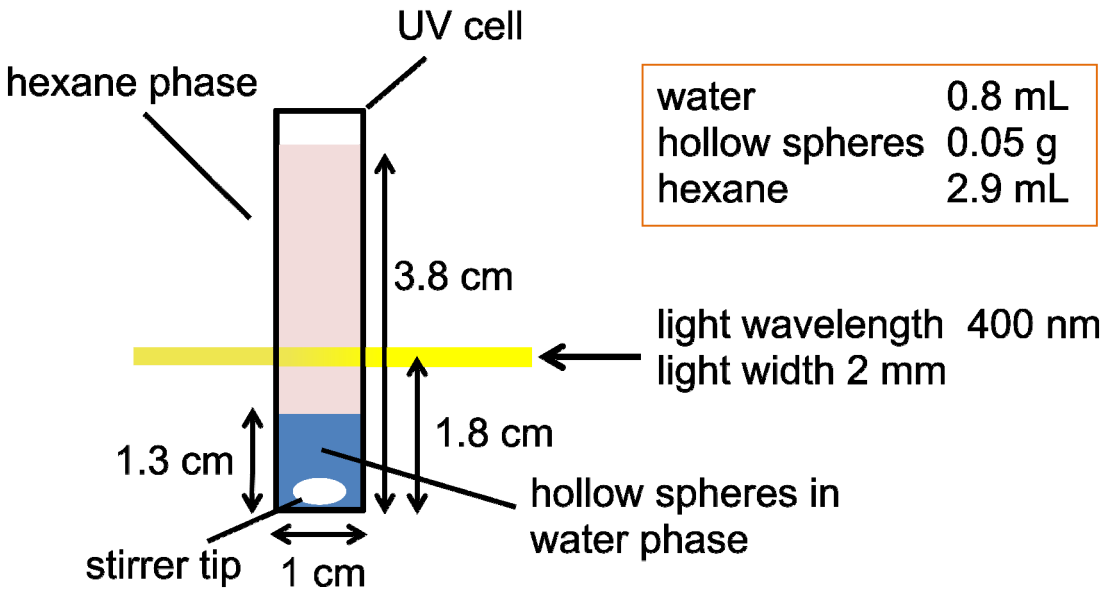

Figure S13 Apparatus for measurement of the amount of the spheres existing in hexane phase during stirring the mixture of two phases

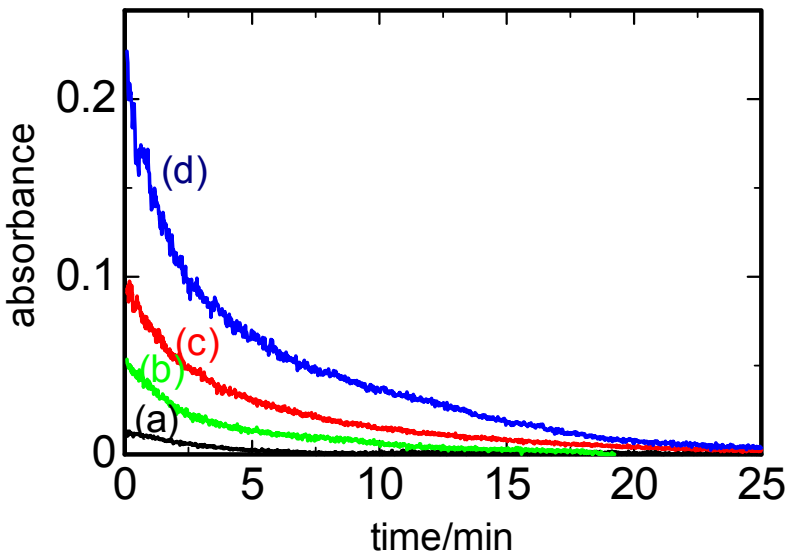

Fig. S14 Time courses of absorbance of hexane phase using a UV light at 400 nm of wavelength after stopping the stirring of water phase containing hollow mesoporous silica spheres modified with organic groups and hexane phase at 1200 rpm for 1 min.

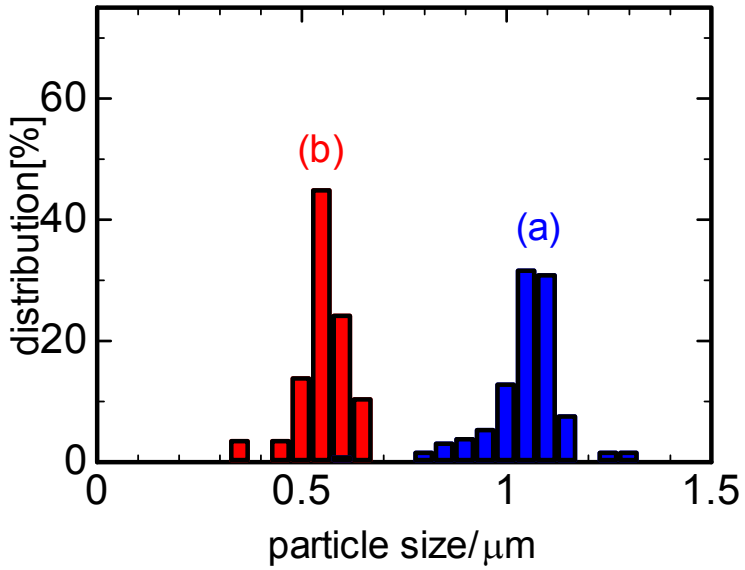

Figure S15 Distributions of particle size (a) and core particle size (b) of rattle-type mesoporous silica spheres with sulfonic acid.

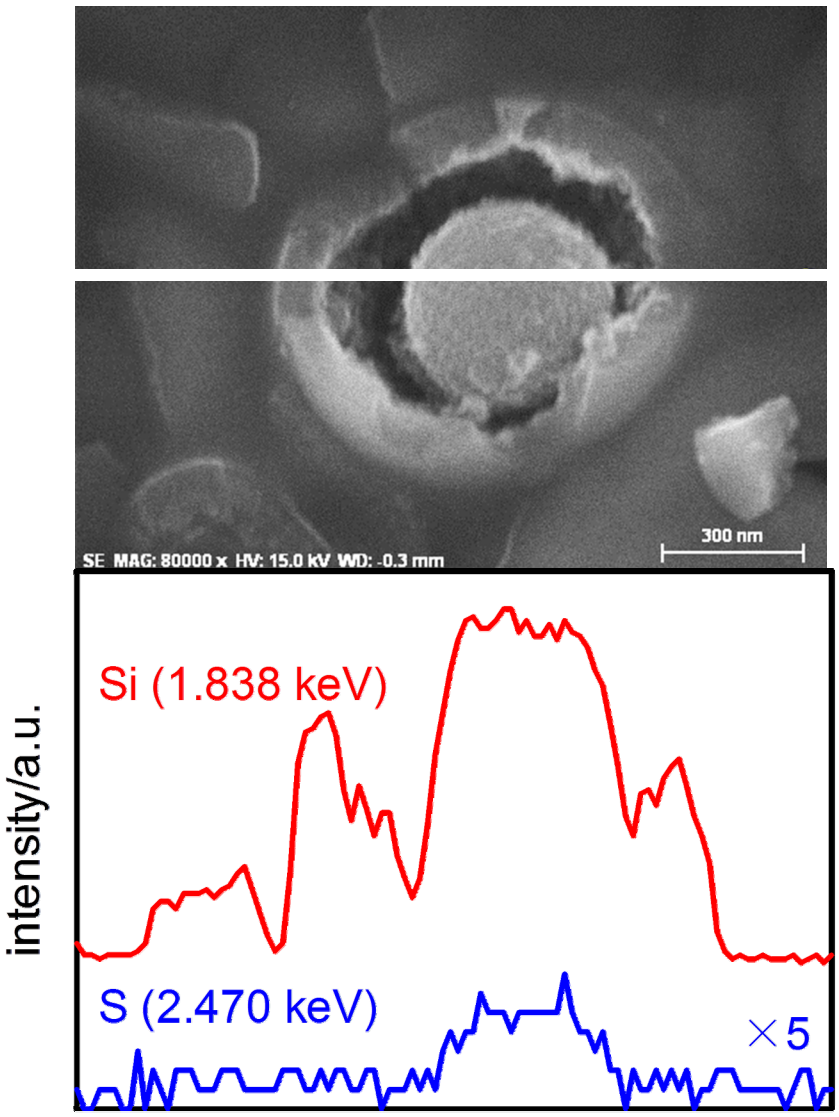

Fig. S16 Elemental analysis of the broken sphere by line scan. Analysis was performed on a white line in SEM image.

Table S1 Characteristics of the mesoporous silica spheres treated with a basic solution

Treatment conditions[a]	Particle size/μm	Pore size/nm	Mesopore volume/mL g^{-1}	Specific surface area/m^2 g^{-1}	d_{100}/nm	Weight loss at 800 °C [wt.%][b]
Before treatment	1.6	1.6	0.37	924	3.6	-
No surfactant	1.3	1.4	0.62	952	3.3	4.4
$6.25x10^{-5}$ M C_{16}TMACl	1.4	1.5	0.67	1077	3.4	n.d.[c]
$1.25x10^{-4}$ M C_{16}TMACl	1.4	1.4	0.59	1056	3.4	10.3
$2.50x10^{-4}$ M C_{16}TMACl	1.4	1.7	0.89	1267	3.4	n.d.[c]
$1.25x10^{-4}$ M C_{12}TMACl	1.4	1.7	0.71	906	3.4	8.0
$1.25x10^{-4}$ M C_{18}TMACl	1.4	1.4	0.45	946	3.4	11.0
$1.25x10^{-4}$ M sodium hexadecylsulfonate	1.4	1.4	0.56	829	3.3	5.1
$1.25x10^{-4}$ M NH_4Cl	1.3	1.4	0.50	881	3.2	4.6

[a]1.0 M ammonia solution, 25 °C, [b]thermogravimetric analysis, [c]not determined.

Table S2 Acid amount and sulfur content of rattle-type mesoporous silica spheres with sulfonic acid.

Rattle-type spheres	Sulfonic acid amount/mol g^{-1}-SiO_2	Sulfur content/mol g^{-1}-SiO_2[a]
Before oxidation	-	$3.6 x10^{-4}$
After oxidation	$2.7x10^{-4}$	$3.2 x10^{-4}$

[a]determined by elemental analysis