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Investigation of pore-size effects on base catalysis using amino-functionalized monodispersed mesoporous silica spheres as a model catalyst

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Abstract

The effects of pore size on base catalysis have been studied using amino-functionalized monodispersed mesoporous silica spheres (NH_2-MMSS). By changing the surfactant that is used for the template and also the synthetic conditions, NH_2-MMSS with similar particle diameters (560–600 nm) and different pore sizes (0–2.66 nm) were successfully prepared. Because the NH_2-MMSS that were obtained had the same shapes, particle diameters and mesopore alignments, any differences in catalytic activity could be substantially attributed to differences in their pore sizes. We employed the nitroaldol condensation between benzaldehyde derivatives and nitromethane as a base catalysis reaction. It was found for the first time that the reaction mostly proceeds inside the mesopores (the effectiveness factor: 0.63) and that the optimum pore size for the NH_2-MMSS was affected by changing the type and number of the substituent groups on the reactants. In addition, NH_2-MMSS was found to be an excellent catalyst due to the radial alignment of the mesopores compared to the other types of mesoporous silica.

Keywords: Mesoporous silica; Monodispersed spheres; Amino-functionalized; Pore size; Base catalyst

1. Introduction

In recent years, various ordered mesoporous materials have been synthesized by using surfactants as templates. Mesoporous silica materials with uniform pore sizes, high surface areas and high concentrations of surface hydroxyl groups are of considerable research interest in fields such as catalysis, adsorption, separation, ion exchange and sensor design. In particular, their application as heterogeneous catalysts is of great interest from the view point of "green" chemistry. In general, heterogeneous catalysts have advantages in terms of separation and regeneration from reaction solutions.

There have been several investigations into the effect of pore size on catalytic activity using mesoporous silica with irregular shapes [1–3]. Iwamoto et al. studied the catalytic activity of various MCM-41 with different pore sizes for the acetalization of cyclohexanone with methanol. They showed that the catalytic activity was strongly dependent on the pore size of the catalysts, and was maximized when the pore size was around 1.9 nm. Because the diameters of cyclohexanone and the product were 0.75 and 0.96 nm, respectively, the phenomenon could not be explained by the concept of shape-selective catalysis. They also reported that the catalytic activity was not dependent on the molecular size of the reactant, but on the pore size of the catalyst [2].

Tanchoux et al. demonstrated that a sharp increase in catalytic activity for the double bond isomerization of 1-hexene was observed for MCM-41 with a pore size of 3.4 nm. They reported that this result was caused by a compensation effect between diffusion limitations and confinement activity enhancement [3]. It became clear that MCM-41 had the optimum pore size in acid catalytic reactions.

However, because the mesoporous silicas that have previously been used as catalysts have had irregular shapes and pore

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arrangements, it is quite difficult to accurately evaluate the effect of pore size on the catalytic activity without any influence from other effects. In order to accurately study the effect of the pore size of the mesoporous silica catalyst on catalytic activity, it is essential to use porous materials that have the same shapes, sizes and pore arrangements.

In our laboratory, we have succeeded in the synthesis of hexagonally ordered and well-defined highly monodispersed mesoporous silica spheres (hereafter abbreviated as "MMSS") from tetramethoxysilane (TMOS) and n-alkyltrimethylammonium halide (C_nTMAX, $X = \mathrm{Cl, Br}$) [4–6]. Because these MMSS have radially aligned mesopores [6], it is expected that accessibility for reactants and the release of products would be enhanced if they were used as catalysts.

Recently, aminopropyl-functionalized mesoporous silica materials such as MCM, FSM, and SBA have been reported to be effective as base catalysts for Knoevenagel condensations [7–10], aldol condensations [11–14], Michael additions [10,11,15] and epoxidation reactions [16].

We synthesized MMSS that were particles with almost the same diameters and different pore sizes. These were functionalized as base catalysts by incorporating an aminopropyl group using a grafting method. The purpose of this work is to understand the "pure" effect of pore size on base catalysis when using amino-functionalized MMSS as a model catalyst.

When a reaction is conducted with micro/meso-porous catalysts, diffusion could govern the reaction because the sizes of reactants and pores are relatively very close [17]. To date, there have been many reports using mesoporous silica as a catalyst. However, in many cases, it has been expected that only a part of mesopores works as a catalyst due to diffusion limitation. Therefore, it is very interesting to know the effectiveness factor of mesoporous silica as a catalyst. This can be only realized by using MMSS with the same pore size and different particle diameter as a catalyst.

We have synthesized five types of amino-functionalized MMSS with almost the same particle diameters and different pore sizes by changing the template surfactant and the synthetic conditions, and their base catalytic performances were evaluated. It was found that the optimum pore size changed depending on the molecular structure of the reactant. We have also conducted a reaction with amino-functionalized MMSS with the same pore size and different particle diameters. The effectiveness factor of spherical mesoporous silica was evaluated for the first time.

2. Experimental

2.1. Chemicals and catalyst synthesis

We synthesized MMSS with the same particle diameters and different pore sizes by using n-alkyltrimethylammonium halide (C_nTMAX: $n = 10$–18, $X = \mathrm{Cl, Br}$) as a templating agent and a tetramethoxysilane (TMOS) as a silica source [5,6]. The particle sizes of the MMSS were adjusted by changing the methanol/water ratio in the solvent.

The amino-moieties were incorporated by a grafting method, in which organically functional groups were attached onto the silica surface via a reaction between the hydroxyl groups on the surface of the mesoporous silica and silane compounds.

3-Aminopropyltrimethoxysilane (APTMS), 4-hydroxybenzaldehyde, 4-butoxybenzaldehyde, 4-n-octoxybenzaldehyde, 4-methoxybenzaldehyde, 2,4,6-trimethoxybenzaldehyde and 3,4,5-trimethoxybenzaldehyde were purchased from Aldrich. Decyltrimethylammonium bromide (C_{10}TMABr), tetradecyltrimethylammonium chloride (C_{14}TMACl), hexadecyltrimethylammonium chloride (C_{16}TMACl), octadecyltrimethylammonium chloride (C_{18}TMACl), and tetramethoxysilane (TMOS) were purchased from Tokyo Kasei. Dococyltrimethylammonium chloride (C_{22}TMACl) was purchased from Lion Akzo Co., Ltd. 1 M sodium hydroxide solution, methanol, hydrochloric acid, dry toluene, nitromethane, tetrahydrofuran (THF), acetone-d_6 and decane were purchased from Wako Inc. Monodispersed silica spheres were purchased from Nippon Shokubai Co., Ltd. All of the chemicals were used as-received.

The syntheses were carried out under basic conditions, as follows.

For example, in the case of C_{16}-MS, 7.04 g of C_{16}TMACl and 6.84 ml of 1 M sodium hydroxide solution were dissolved in 1600 g of a methanol/water ($50/50 = \mathrm{w/w}$) solution (methanol ratio: 0.5). 5.28 g (34.7 mmol) of TMOS was added to the solution with vigorous stirring at 298 K. After the addition of the TMOS, the clear solution suddenly turned opaque and resulted in a white precipitate. After 8 h of continuous stirring, the mixture was aged overnight. The white powder was then filtered and washed three times with distilled water, after which it was dried at 318 K for 72 h. The powder that was obtained was calcined in air at 823 K for 6 h to remove the organic species.

In the case of pore-expanded MMSS (C_{18}PS-MS), 2 g of C_{18}-MS before calcination was suspended in 120 g of a 0.1 M C_{22}TMACl water–ethanol solution. The mixture was sealed and placed in an oven at 353 K for 7 days without stirring. The resulting white powder was filtered and washed with distilled water and then dried. The powder that was obtained was calcined in air at 823 K for 6 h to remove the organic species.

Amino moiety grafting was performed on calcined and evacuated (323 K) samples of MMSS, on FSM [18] and on nonporous monodispersed silica spheres (SS).

For example, in the case of C_{16}-MS-AP, 0.7 g of calcined C_{16}-MS was added to a mixture of 70 g of dehydrated toluene and 1.88 g of APTMS, and the solution was then refluxed at 363 K for 15 h. The product was dried overnight at 318 K after filtration.

Hereafter in this paper, the samples that were obtained are abbreviated as C_xPS-MS, where x is 10, 14, 16 or 18. x denotes the number of carbon atoms of alkyl chain in the surfactant that was used as a templating agent, and PS indicates that the pore size of the material was expanded by the surfactant exchange method [19]. Amino-functionalized materials are denoted by attaching "AP" to the end of the sample names.

2.2. Sample characterization

Powder X-ray diffraction measurements were carried out on a Rigaku Rint-2200 X-ray diffractometer using Cu$K\alpha$ radiation. Scanning electron micrographs (SEMs) were obtained using a Sigma-V (Akashi Seisakusho). The surfaces of the samples were coated with gold before the measurements. The average particle diameter was calculated from the diameters of 50 particles in an SEM picture. The standard deviation was also calculated, from which the distribution of the particle diameters was derived. The nitrogen adsorption isotherms were measured using a Belsorp-mini II (BEL Japan) at 77 K. The samples were evacuated at 373 K under 10^{-3} mmHg before measurement. The pore diameters were calculated using the Barrett–Joyner–Halenda (BJH) method. By considering the linearity of a Brunauer–Emmett–Teller (BET) plot, the specific surface areas were calculated using adsorption data in the P/P_0 range from 0.05 to 0.13. Transmission electron micrographs were obtained using a Jeol-200CX TEM at an acceleration voltage of 200 kV. ^{29}Si magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) and ^{13}C cross-polarization (CP) NMR analyses were carried out on a Bruker AVANCE 400 spectrometer at 79.49 MHz for ^{29}Si and at 100.61 MHz for ^{13}C. The ^{29}Si MAS NMR spectra were measured at 60 s repetition delay and 3 µs pulse width. The ^{13}C CP MAS NMR spectra were measured at 2 s repetition delay, 2 ms contact time, and 2.8 µs ^{1}H 90° pulse. The chemical shifts for ^{29}Si and ^{13}C NMR were referenced to tetramethylsilane and glycine, respectively. For both measurements, the spinning rate was 5 kHz. N elemental analyses (EA) were carried out on an Elementer vario EL elemental analyzer.

2.3. Catalytic reactions

Reactions were carried out in a round-bottomed flask equipped with a reflux condenser. The nitroaldol condensation was typically carried out as follows: a reaction mixture consisting of 50 mg of the catalyst and 0.61 g (5.0 mmol) of 4-hydroxybenzaldehyde in 10 ml of nitromethane was heated at 363 K with constant stirring for 1 h. The mixture was filtered and the catalyst on the filter was washed thoroughly with chloroform. The filtrate was evaporated under reduced pressure. The solid that was obtained was completely dissolved in a sufficient amount of acetone-d_6. An internal standard, THF ($\approx$10 mmol), was added into the acetone-d_6 solution. The product was analyzed by studying its ^{1}H NMR spectra on a Jeol JNM-LA500 NMR spectrometer [14].

In case when 4-methoxybenzaldehyde was used as a reactant, the reaction was monitored periodically by withdrawing an aliquot of solution from the solution in order to determine a reaction rate. The samples were filtered and analyzed by gas chromatograph (Agilent, 6890) provided with a 30 m capillary column of DB-1, using decane as an internal standard for mass balance. These products were characterized by MS (Agilent, 6890-5973) provided with a 30 m capillary column of DB-5MS. In order to compare reaction rates of various MMSS, we evaluated TOF (turn over frequency) from the data for the reaction time of 10 min.

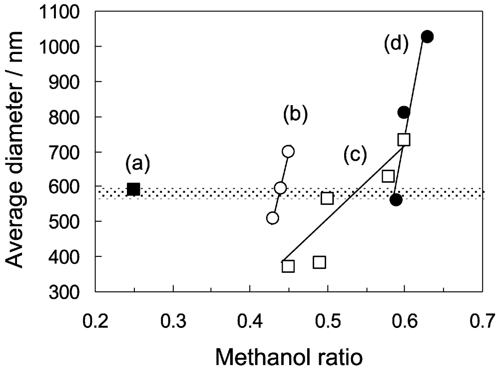


Fig. 1. Relationship between the methanol ratio and average particle diameter of MMSS obtained using quaternary ammonium salts with different alkyl-chain lengths. (a) C_{10}TMABr, (b) C_{14}TMACl, (c) C_{16}TMACl and (d) C_{18}TMACl.

3. Results and discussion

3.1. Synthesis of MMSS with the same particle diameters and different pore sizes

In order to clarify the relationship between the pore size of a mesoporous silica catalyst and its catalytic activity, the provision of MMSS samples with the same particle diameters and different pore sizes is necessary.

We have previously succeeded in the synthesis of MMSS with different pore sizes by using various surfactants as templates. However, no attempts have been made to synthesize MMSS with the same particle diameters. From a previous report [6], it is obvious that the particle diameter of MMSS tends to increase as the number of carbon atoms in the surfactant increases. To overcome this tendency, the requirement for precise control of the reaction conditions during MMSS synthesis is essential. Because the particle diameter of the MMSS is significantly affected by the methanol ratio in the solvent [5], syntheses were conducted under various methanol ratios. Fig. 1 shows the relationship between the methanol ratio and the average particle diameter of MMSS samples obtained from quaternary ammonium salts with different alkyl-chain lengths (C_{10}TMABr, C_{14}TMACl, C_{16}TMACl, C_{18}TMACl). The methanol ratios with which the monodispersed particles were obtained changed drastically depending on the type of surfactant that was used. Although C_{16}-MS (MMSS synthesized using C_{16}TMACl as a template) could be obtained over a wide methanol ratio range (0.45–0.6), C_{14}-MS and C_{18}-MS were only obtained in narrow methanol ratio ranges. It was found that by precisely controlling the methanol ratio, MMSS samples with almost the same particle diameters could be obtained using quaternary ammonium salts with different alkyl-chain lengths.

3.2. Characterization of C_x-MS-AP

Amino-functionalized MMSS samples were obtained by grafting APTMS onto C_x-MS. Fig. 2 shows SEM images of C_x-MS-AP. As can be seen from Fig. 2, the particles were highly monodispersed, and their average particle diameters

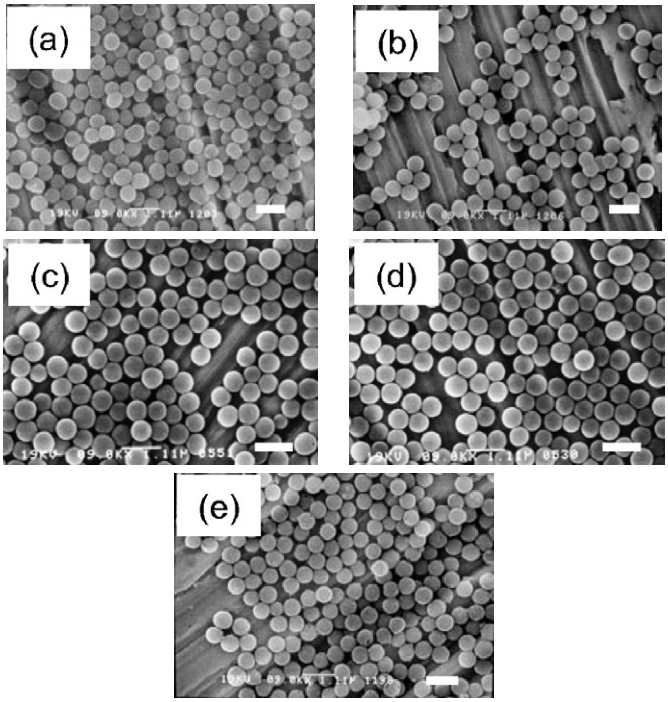


Fig. 2. Scanning electron micrographs of (a) C_{10}-MS-AP, (b) C_{14}-MS-AP, (c) C_{16}-MS-AP, (d) C_{18}-MS-AP and (e) C_{18}PS-MS-AP. Scale bar represents 1.1 µm.

were between 560 and 600 nm. Table 1 summarizes the synthetic conditions and properties of the particles. The regularity of the mesopores was studied by X-ray diffraction measurements (Fig. 3). The peak intensities of d_{100} for all samples except for C_{10}-MS-AP were over 10,000, indicating that the C_x-MS-AP had well-ordered hexagonal regularity. In the case of C_{10}-MS-AP, the intensity of d_{100} was very low. It is considered that because most of the mesopores of C_{10}-MS were filled with amino-moieties, the contrast between the mesopores and the silica walls became less, leading to low d_{100} intensity. From the XRD results shown in Table 1, it was confirmed that the value of d_{100} increased with increasing alkyl-chain length of the surfactant.

The nitrogen adsorption–desorption isotherms were measured and the pore-size distributions were analyzed by the BJH method. Fig. 4 shows the results for C_x-MS-AP samples. The

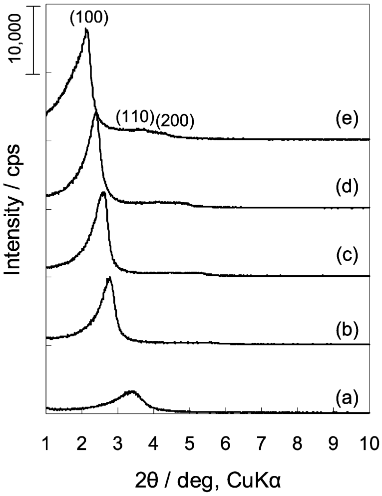


Fig. 3. XRD patterns of the samples: (a) C_{10}-MS-AP, (b) C_{14}-MS-AP, (c) C_{16}-MS-AP, (d) C_{18}-MS-AP and (e) C_{18}PS-MS-AP.

isotherms of the samples are similar to those without organically functional groups (MMSS) [6], but C_{10}-MS-AP hardly adsorbed any nitrogen. This result agreed well with the result from the XRD measurements. Most of the mesopores in C_{10}-MS-AP were filled with amino-moieties. As with the results of the XRD measurements, the pore sizes of C_x-MS-AP increased as the alkyl-chain length of the surfactant increased. C_{18}PS-MS-AP that was synthesized from pore-expanded C_{18}PS by the surfactant exchange method had the largest pore size of 2.66 nm (Table 1).

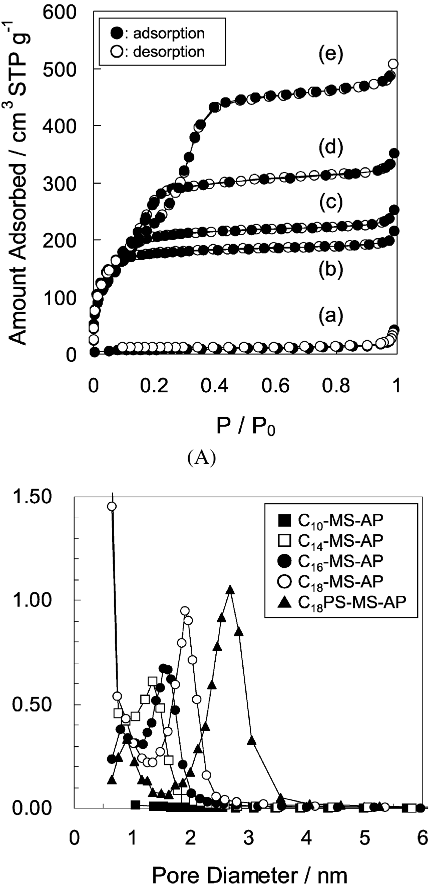
The N contents of the samples are also shown in Table 1. Although the N content of C_{18}PS-MS-AP (which has the greatest pore size) was a little larger (2.1 mmol/g), most of the samples had almost the same N content (1.71–1.82 mmol/g), indicating that nearly equal amounts of amino groups were incorporated into MMSS samples with different pore diameters.

For comparison, grafting of amino-moieties was conducted for FSM-16, which is mesoporous silica having irregular shape, and monodispersed silica spheres without pores. They are denoted as FSM-16-AP and SS-AP hereafter. FSM-16-AP had the pore size of 1.98 nm which was little bit larger than C_{18}-MS-AP and N content of 1.74 mmol/g. SS-AP had almost the same particle diameter of MMSS samples (550 nm).

Table 1
Properties of aminopropyl-functionalized MMSS

Sample	Surfactant concentration (mM)	Methanol ratio	Average diameter (nm)	Standard deviation (%)	XRD		Nitrogen adsorption			N content (mmol/g)
					d_{100} (nm)	Intensity (cps)	Pore size (nm)	S_{BET} (m^2/g)	Pore volume (ml/g)	
C_{10}-MS-AP	13.7	0.25	590	10.1	2.56	3400	–	280	0.03	1.71
C_{14}-MS-AP	13.7	0.44	600	5.4	3.18	10,100	1.34	730	0.31	1.79
C_{16}-MS-AP	13.4	0.50	580	6.2	3.36	12,500	1.53	870	0.40	1.78
C_{18}-MS-AP	13.8	0.59	560	6.3	3.67	14,500	1.89	850	0.50	1.82
C_{18}PS-MS-AP[a]	–	–	590	5.6	4.09	16,200	2.66	810	0.74	2.10
FSM-16-AP	–	–	–	–	3.71	8900	1.98	600	0.41	1.74
SS-AP			550	4.0						0.13

[a] This was obtained by aminopropyl grafting on pore-expanded MMSS [19].



(A)

(B)

Fig. 4. (A) Nitrogen adsorption–desorption isotherms and (B) pore-size distributions of (a) C_{10}-MS-AP, (b) C_{14}-MS-AP, (c) C_{16}-MS-AP, (d) C_{18}-MS-AP and (e) C_{18}PS-MS-AP.

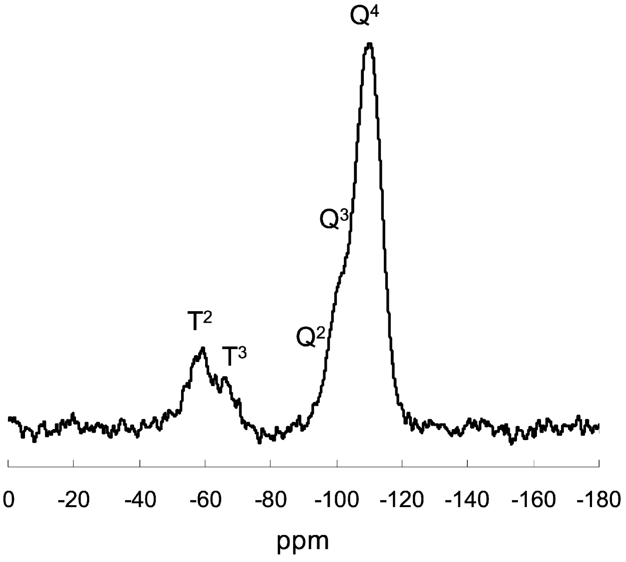


Fig. 5. ^{29}Si MAS NMR spectrum of C_{16}-MS-AP.

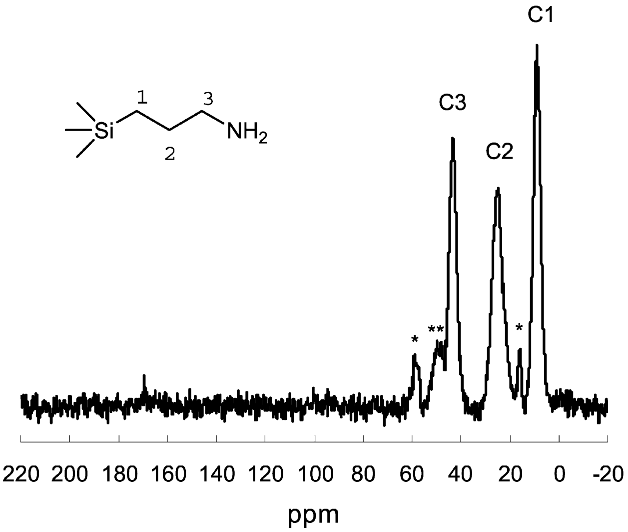


Fig. 6. ^{13}C CP MAS NMR spectrum of C_{16}-MS-AP. (* Signals from residual ethoxy group. ** Signals from residual methoxy group.)

The ^{29}Si and ^{13}C CP MAS NMR spectra of C_{16}-MS-AP were measured and its chemical structure was investigated (Figs. 5 and 6). In the ^{29}Si MAS NMR spectrum, three clear resonance peaks derived from Q^n ($Q^n = \mathrm{Si(OSi)}_n\mathrm{(OH)}_{4-n}$, $n = 2$–4, Q^4: $\delta = -110$ ppm, Q^3: $\delta = -100$ ppm, Q^2: $\delta = -92$ ppm) and two peaks derived from T^m ($T^m = \mathrm{RSi(OSi)}_m\mathrm{(OH)}_{3-m}$, $m = 1$–3, T^3: $\delta = -65$ ppm, T^2: $\delta = -57$ ppm) were observed. The spectrum that was obtained is the same as those of organically functionalized SBA-15 or MCM-41 obtained by the grafting method [20,21]. The presence of the T^m peaks indicated the incorporation of amino-moieties into the silica skeleton. In the ^{13}C CP MAS NMR spectrum, peaks derived from the C atoms of the incorporated aminopropyl groups were observed. This result also supports the conclusion that amino-moieties were successfully incorporated into the mesopores. Other than main peaks, there are some small peaks observed. Two small peaks at $\delta = 59$, 16 ppm were assigned to the ethoxy carbon atoms assumed to be generated by the partial esterification of the surface silanol with ethanol which was used as solvent for washing [22]. A small peak at 50 ppm was assigned to unreacted methoxy carbon atoms of organic trimethoxysilane [23].

The radial alignment of the mesopores was confirmed by TEM observations (Fig. 7). It was observed that the hexagonal mesopores were arrayed in a radial pattern [19,24].

These experimental results led us to the conclusion that five types of amino-functionalized MMSS with nearly the same particle diameters and different pore sizes had been successfully prepared.

3.3. Evaluation of catalytic activity

The catalytic activities of C_x-MS-AP were studied by the nitroaldol condensation of nitromethane and benzaldehyde derivatives. Firstly, 4-methoxybenzaldehyde was used as the reactant. Fig. 8 shows time course of yields of nitroaldol condensation of nitromethane and 4-methoxybenzaldehyde using C_{14}-MS-AP, C_{18}-MS-AP, and FSM-16-AP as a catalyst. Table 2 summarizes initial rate and TOF (turnover frequency, min^{-1}) determined from data for 10 min reaction, and TON (turnover number) determined from data for 1 h reaction for various cat-

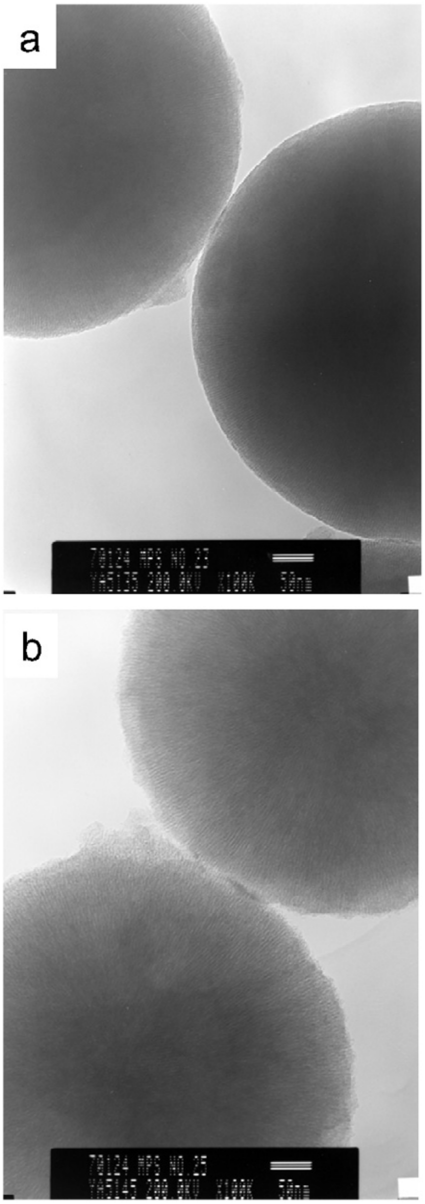


Fig. 7. Transmission electron micrographs of (a) C_{16}-MS-AP and (b) C_{18}PS-MS-AP. Scale bar represents 50 nm.

Table 2
Results of nitroaldol condensations of 4-methoxybenzaldehyde with nitromethane in the presence of catalyst (363 K)

Catalyst	Initial rate (mmol g_{cat}^{-1} min^{-1})	Initial TOF[a] (min^{-1})	TON[b] (yield, %)
C_{10}-MS-AP	0	0	3 (5)
C_{14}-MS-AP	1.8	1.0	41 (74)
C_{16}-MS-AP	2.3	1.3	54 (96)
C_{18}-MS-AP	2.2	1.2	52 (94)
C_{18}PS-MS-AP	2.2	1.0	44 (92)
FSM-16-AP	1.3	0.8	52 (90)

[a] Turnover frequency = mmol product/mmol organic groups during initial 10 min. TOF was determined by GC analysis.

[b] Turnover number = mmol product/mmol organic groups during 1 h. TON was determined by NMR analysis.

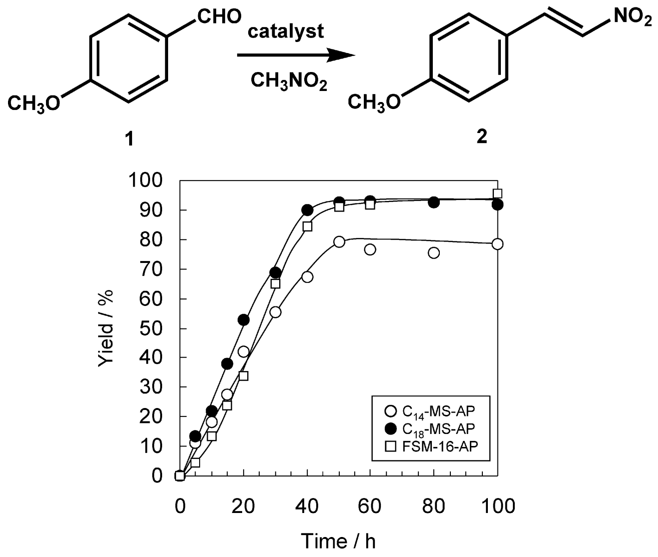


Fig. 8. Changes in the activity of various types of catalysts in nitroaldol condensation reaction.

alysts. From Fig. 8 it is obvious that most of the reactions finished just before 1 h. These results indicate that comparison of their catalytic activity by the use of TON determined from the data for 1 h reaction is appropriate for this reaction system. In order to determine reaction rates, we used GC for analysis. However, yields determined by GC fluctuated and we used NMR for determining TON, because the data obtained from NMR is more reliable than the data from GC due to poor volatile property of the product. It turned out that the initial TOF and TON largely affected by the pore size of MMSS. C_{16}-MS-AP (pore size: 1.53 nm) and C_{18}-MS-AP (pore size: 1.89 nm) showed high catalytic activity. Initial TOF values of these samples were 1.3 and 1.2 min^{-1}, which were higher than the values for the other catalyst. The final yields of these samples were also higher than those of the other catalysts, indicating that initial TOF and TON correlated well for C_x-MS-AP samples. Meanwhile, amino-grafted FSM-16 (pore size: 1.98 nm) showed smallest initial TOF of 0.8 min^{-1}. However, yield increased gradually, and the final TON became almost the same value with that of C_{18}-MS-AP. FSM-16 is mesoporous silica having an irregular shape, and most of mesopores are aligned in the same direction. This means that most of its outer surface is covered with silica walls, leading to limited access for the reactants. On the contrary, in MMSS, the mesopores are aligned radially from the center to the outside of a particle. Therefore, reactants can enter into the mesopores from all directions. It may be concluded that C_x-MS-AP is one of the best catalysts for the nitroaldol reactions of benzaldehyde derivatives among other mesoporous silicas.

It turned out that the catalytic activity was affected by the pore size of MMSS, that is, the reaction is not in totally diffusion control. If sizes of mesopores are close to the sizes of reactants, a reaction could be mainly controlled by diffusion. In this case, a product is generated mostly on the surface of a catalyst. Therefore, it is very important to know what percentage of mesopores is effectively used for the reaction. Then, the effec-

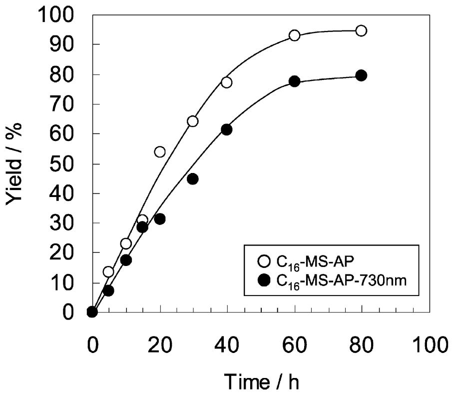
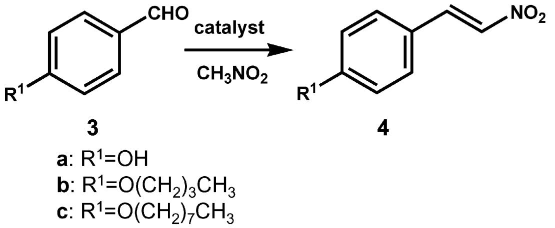


Fig. 9. Changes in the activity of MMSS catalyst having different particle diameter in nitroaldol condensation reaction.

Table 3

Results of nitroaldol condensations of 4-substituted benzaldehyde with nitromethane in the presence of C_x-MS-AP catalyst (363 K, 1 h)



Catalyst	Yield (%)			TON[a]		
	a	b	c	a	b	c
C_{10}-MS-AP	2	4	4	1	2	2
C_{14}-MS-AP	52	49	55	29	27	31
C_{16}-MS-AP	86	100	92	48	⩾56	52
C_{18}-MS-AP	78	98	86	43	54	47
C_{18}PS-MS-AP	75	98	91	36	47	43
C_{16}-MS	0	–	–	0	–	–
SS-AP	5	–	–	38	–	–

[a] Turnover number = mmol product/mmol organic groups during 1 h.

tiveness factor of MMSS was evaluated from the kinetic data measured by use of catalysts with different particle diameters but the same pore size. Fig. 9 shows time course of yields of nitroaldol condensation of nitromethane and 4-methoxybenzaldehyde using C_{16}-MS-AP (particle diameter: 580 nm) and C_{16}-MS-AP-730nm (particle diameter: 730 nm). Initial rates determined from the reaction time of 10 min for C_{16}-MS-AP and C_{16}-MS-AP-730 nm were 2.3 and 1.8 mmol g_{cat}^{-1} min^{-1}, respectively. From these rate and particle diameter data, the effectiveness factor of MMSS was evaluated to be 0.63. This result suggests that MMSS with smaller particle diameter could be a candidate for an ideal catalyst or catalyst support because higher effectiveness factor can be expected for smaller particles.

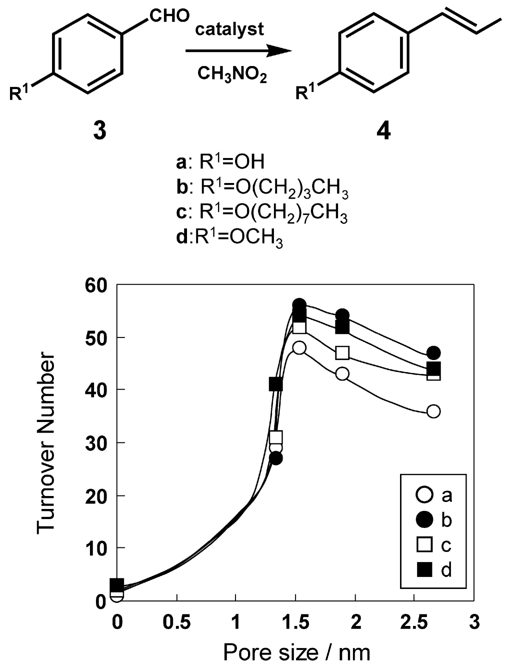


Fig. 10. Relationship between the pore size of particles and turnover number for nitroaldol condensation. The pore size of C_{10}-MS-AP was estimated to be zero from the nitrogen adsorption measurement.

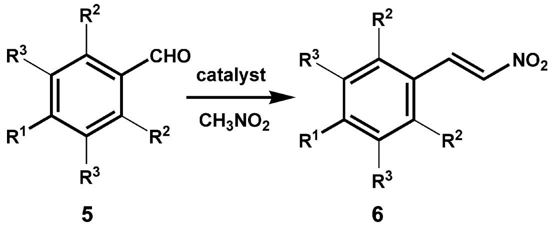
3.4. Influence of molecular size

In order to investigate the effect of the molecular size of the reactant on the catalytic activity, firstly, *para*-benzaldehyde derivatives incorporating alkoxy groups with different alkyl-chain lengths were examined. Products for 1 h reaction were analyzed, and yields and TON were determined. Table 3 shows the results obtained from the reaction between nitromethane and 4-hydroxybenzaldehyde (**3a**). MMSS without any amino groups (C_{16}-MS) showed no catalytic activity, suggesting that it is the amino-moieties that act as catalysts. The yield increased as we increased the pore size of the C_x-MS-AP, and reached a maximum (86%) for C_{16}-MS-AP. C_{10}-MS-AP showed very low catalytic activity; its yield was 2% and its TON was 1. Because the mesopores of C_{10}-MS-AP are considered to be filled with amino-moieties, the reactants could not reach the active sites (= amino-moieties) inside the mesopores. When C_{14}-MS-AP (pore size: 1.34 nm) or C_{16}-MS-AP (1.53 nm) were used as the catalysts, the TON increased to 29 or 48, respectively. It became clear that the mesopores require a certain capacity for the enhancement of catalytic activity. However, when C_{18}-MS-AP (pore size: 1.89 nm) or C_{18}PS-MS-AP (2.66 nm), which have larger mesopores, were used as catalysts, the TON decreased to 43 or 36, respectively. Meanwhile, when SS-AP, which has nearly the same particle diameter with MMSS samples and no mesopores, was used as a catalyst, the yield was as low as 5%. This result strongly supports the assumption that the reaction occurred mainly in mesopores, but outer surfaces. Fig. 10 shows the relationship between the pore size of the samples and the TON for the reaction. The pore size of C_{10}-MS-AP was estimated to be zero from the result of the nitrogen adsorption measurement. It can be seen from Fig. 10 that there is an optimum pore size for the reaction. In Fig. 10, results obtained when 4-methoxybenzaldehyde was used as a reactant were also shown and the tendency was the same with the results for the other reactants.

Then, the study was conducted by using *para*-substituted reactants with longer substituents. The reactants that were used were 4-butoxybenzaldehyde (**3b**) and 4-*n*-octoxybenzaldehyde

Table 4

Results of nitroaldol condensations of multi-substituted benzaldehyde with nitromethane in the presence of C_x-MS-AP catalyst (363 K, 1 h)



a: $R^1=OCH_3$, $R^2=H$, $R^3=H$
b: $R^1=R^2=OCH_3$, $R^3=H$
c: $R^1=R^3=OCH_3$, $R^2=H$

Catalyst	Yield (%)			TON[a]		
	4-OMe **a**	2,4,6-OMe **b**	3,4,5-OMe **c**	4-OMe **a**	2,4,6-OMe **b**	3,4,5-OMe **c**
C_{10}-MS-AP	5	21	1	3	12	1
C_{14}-MS-AP	74	69	27	41	39	15
C_{16}-MS-AP	96	62	77	54	35	43
C_{18}-MS-AP	94	83	88	52	46	48
C_{18}PS-MS-AP	92	75	90	44	36	43

[a] Turnover number = mmol product/mmol organic groups during 1 h.

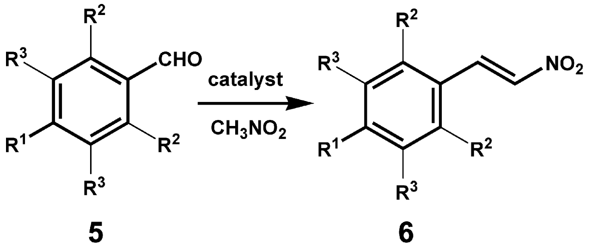
(**3c**). The results of the reactions are also shown in Table 3 and Fig. 10. In all cases, C_{16}-MS-AP exhibited the best catalytic performance among those tested, as seen for 4-hydroxybenzaldehyde and 4-methoxybenzaldehyde. It is surprising that the optimum pore size remained unchanged for the reaction, even though the molecular sizes of the reactants changed drastically. Based on the Molecular Mechanics model, the sizes of the molecules along their longer axes are about 0.67 nm for 4-hydroxybenzaldehyde, 0.82 nm for 4-methoxybenzaldehyde, 1.15 nm for 4-butoxybenzaldehyde, and 1.70 nm for 4-*n*-octoxybenzaldehyde. The pore size of C_{16}-MS-AP as determined from the adsorption measurement was 1.53 nm, which is smaller than the molecular size of 4-*n*-octoxybenzaldehyde on its longer axis. However, all of the benzaldehyde derivatives had the same molecular size, ca. 0.43 nm, for their shorter axes. It is assumed that the benzaldehyde derivatives entered into mesopores parallel to the pore directions and reacted with the amino groups that existed inside mesopores. The pore size of C_{16}-MS-AP is considered to be the most suitable for the reaction of amino groups and *para*-substituted aldehyde moieties from the view point of optimal space and density of the amino-moieties.

The size of the substituent group affected the catalytic activities of the C_x-MS-AP samples. When 4-butoxybenzaldehyde (**3b**) was used as the reactant, the value of TON was the highest in many cases, that is, C_x-MS-AP exhibits some selectivity for the reaction [25]. It is thought that hydrophobic environment was formed in the mesopores of MMSS by the incorporation of organically functional groups, leading to easy infiltration of reactants with an alkyl-chain into the mesopores. However, given the diffusion of the reactant, there is an optimum size for the reaction to take place. The optimum pore size was not affected at all by the *para*-substitution of the reactant.

In order to investigate further the effects of the molecular size of the reactant on the catalytic activity, multi-substituted aldehydes such as 2,4,6-trimethoxybenzaldehyde (**5b**) and 3,4,5-trimethoxybenzaldehyde (**5c**) were examined. It is expected that introduction of substituents on *meta* or *ortho* position leads to the change in minimum kinetic diameter [17,26], which brings to the change in an optimum pore size for the reaction. Table 4 and Fig. 11 show the results of the catalytic activities for the reaction. When multi-substituted aldehydes were used as a reactant, C_{18}-MS-AP, which has a pore size of 1.89 nm, exhibited the highest catalytic activity. The optimum pore size for the nitroaldol condensation shifted to higher value by increasing the number of substituent groups in the reactant. The molecular size of the reactants became more bulky as the number of methoxy groups increased, and then the catalytic activity of C_{16}-MS-AP fell sharply. On the contrary, the activity of C_{18}-MS-AP and C_{18}PS-MS-AP hardly changed. The dimensions of the molecule between the 1-position and the 4-position for the longer axis is about 0.82 nm and the shorter axis is 0.43 nm for 4-methoxybenzaldehyde. The shorter axis increases to 0.82 nm for the multi-substituted aldehydes because the methoxy groups are disposed along both sides of the benzene ring. We assume from the foregoing experiments that the aldehydes entered into the mesopores parallel to the pore directions. Larger pores are considered to be necessary to enable more-bulky reactants to enter smoothly into the mesopores.

4. Conclusions

Precise control of the reaction conditions led to the successful synthesis of amino-functionalized monodispersed mesoporous silica spheres with nearly the same particle diameters and different pore sizes or with the same pore size and different particle diameters. By using the amino-functionalized monodispersed mesoporous silica spheres as catalysts, the effect of pore size on base catalysis has been studied. It was found for the



a: R^1=OCH_3, R^2=H, R^3=H
b: R^1=R^2=OCH_3, R^3=H
c: R^1=R^3=OCH_3, R^2=H

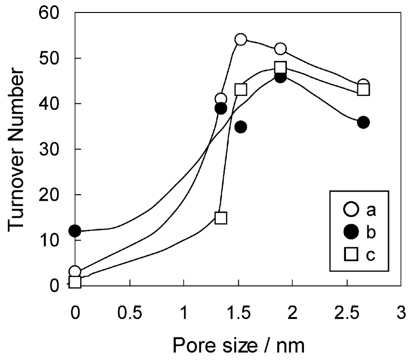


Fig. 11. Relationship between the pore size of particles and turnover number for nitroaldol condensation.

first time that an optimum pore size exists, which changes depending on the size and shape of the reactants. In addition, by changing particle diameter, the effectiveness factor of MMSS was evaluated to be 0.63. Amino-functionalized monodispersed mesoporous silica spheres were found to be excellent catalysts for nitroaldol condensation due to the radial alignment of their mesopores when compared to other types of mesoporous silica, such as FSM-16. Because the amino-functionalized monodispersed mesoporous silica spheres were identical particles except for the sizes of their mesopores, other external causes, such as particle diameter and shape, and mesopore alignment, can be ignored. It is believed that mesoporous materials such as these will be useful as basic research materials for studies of catalysis if a reaction is not under diffusion control. Moreover, by designing the pore properties of the MMSS through the introduction of hydrophobic, hydrophilic, basic, or acidic moieties, this material can now be considered as a candidate for a new type of substrate-selective catalyst.

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