

Direct synthesis of amino-functionalized monodispersed mesoporous silica spheres and their catalytic activity for nitroaldol condensation

Tomiko M. Suzuki^{*}, Tadashi Nakamura, Keiko Fukumoto, Masami Yamamoto,
Yusuke Akimoto, Kazuhisa Yano^{**}

Toyota Central Research & Development Labs Inc., Nagakute, Aichi 480-1192, Japan

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Abstract

New amino-functionalized monodispersed mesoporous silica spheres (MMSS) were synthesized directly by co-condensation of 3-aminopropyltrimethoxysilane (AP-TMS), [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAP-TMS) or 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEAEAP-TMS) with tetramethoxysilane. By changing the methanol ratio or adding extra silica source, amino-functionalized MMSS with different particle diameter (310–780 nm) and the same mesopore size were successfully synthesized. TEM observations revealed that the mesopores were aligned radially from the center towards the outside of the spheres even in the amino-functionalized MMSS. The effect of particle diameter on base catalytic activity was investigated using the amino-functionalized MMSS. In addition, the amino-functionalized MMSS were found to be excellent base catalysts in the nitroaldol condensation reactions. The effectiveness factor was evaluated to be 0.8–0.82 and improved substantially compared with MMSS prepared by grafting method.

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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 expected to be used for catalysts, adsorbents, sensors, separation, and ion exchange columns.

To broaden the applications of mesoporous silica, many researchers have focused on the syntheses of organic–inorganic hybrid materials by incorporating organic functional groups into mesoporous silica [1,2]. In particular, mesoporous silicas that have been modified by amino groups have attracted much attention as useful heterogeneous catalysts in these publications. Recently aminopropyl-functionalized mesoporous silica materials were reported to be effective base catalysts for Knoevenagel condensations [3–6], the aldol condensations [7–9],

Michael additions [6,7,10], epoxidation reactions [11], and Claisen–Schmidt condensations [12]. Furthermore, the development of biomimetic catalysts, in which a metal complex is formed by binding an amino acid to an amino group in mesoporous silica, has been reported [13].

Postsynthesis grafting and co-condensation are general modification methods that have been utilized to attach organic groups to silica surface via the formation of covalent bonds. Grafting can be used to incorporate organic functional groups after the particles are formed. This typically involves reactions between hydroxyl groups on the surfaces of the mesopores and a silane compound. The technique has been widely utilized, and has various merits. The structure of the mesoporous silica particles can be maintained, a wide range of functional groups can be used, and high hydrothermal stability can be achieved [14]. However, it has been noted that the uniform dispersion of organic functional groups is difficult, and the grafting leads to the condensation of organic functional groups near the pore windows causing “pore blocking” [15]. On the other hand, the co-condensation method has a tendency to decrease the degree of mesoporosity as a result of the incorporation of functional groups. Nevertheless, it is still possible to homogeneously incor-

^{*} Corresponding author.

^{**} Corresponding author. Fax: +81 561 63 6507.

E-mail addresses: tomiko@mosk.tytlabs.co.jp (T.M. Suzuki),
k-yano@mosk.tytlabs.co.jp (K. Yano).

porate organic functional groups onto the surface of mesopores [15].

In previous studies into the synthesis of MCM-41 mesoporous silica, attempts to control the morphology of the particles were made for MCM-41 type materials that had been organically functionalized by the co-condensation method. Mann et al. reported that, by changing the organoalkoxysilane or its concentration, spherical, tube-like, rod-like and filament-shaped particles could be obtained. For instance, when 3-aminopropyltrimethoxysilane was used, oblate ellipsoidal particles were obtained [16]. Furthermore, Lin et al. carried out synthesis using lower concentrations of surfactants and rod-shaped particles were obtained with 3-aminopropyltrimethoxysilane and *N*-(2-aminoethyl)-3-aminopropyltriethoxysilane, while spherical particles were obtained when 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane was used [17]. In addition, they found that these spherical particles exhibited some selectivity in base catalysis when secondary organic functional groups were incorporated [18,19].

However, these spherical mesoporous silicas were found to feature lower monodispersity and the array-direction of the mesopores was irregular.

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_n TMAX, $X = \text{Cl, Br}$) [20–22]. By changing the surfactant that is used for the template and also the synthetic conditions, the particle diameters and the pore sizes of MMSS can be controlled flexibly. For fundamental studies of catalytic reactions, the diameters of the particles should be monodispersed. We have been studied the effect of pore size on base catalysis using amino-functionalized MMSS by grafting method. It was found for the first time that the reaction mostly proceeded inside the radially aligned mesopores (the effective factor: 0.63) and that the optimum pore size for amino-functionalized MMSS was affected by changing the type and the number of the substituent groups on the reactants. In addition, amino-functionalized MMSS was found to be an excellent catalyst due to the radial alignment of the mesopores compared to the other types of mesoporous silica [23].

In this study, we attempted to synthesize functionalized MMSS using a co-condensation method to incorporate various amino groups. Compared with the grafting method, it can be expected that the distribution of amino groups becomes homogeneously and the catalytic activity improves.

As a result, we have succeeded in obtaining amino-functionalized monodispersed spherical particles that contain radially aligned mesopores. We also confirmed that they show high base catalytic activities. By controlling the conditions used for the syntheses, MMSS particles of different sizes but with the same diameter of pores were synthesized.

It was found that the effectiveness factor improved greatly compared with the particle prepared by grafting method.

2. Experimental

2.1. Chemicals and catalyst synthesis

We synthesized amino-functionalized MMSS by using hexadecyltrimethylammonium chloride (C_{16} TMACl) as a template for a co-condensation reaction between tetramethoxysilane (TMOS) and organic trimethoxysilane (R-TMS). Three different types of organic trimethoxysilanes were used: 3-aminopropyltrimethoxysilane, $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ (AP-TMS), which contains just one amino group, [3-(2-aminoethylamino)propyl]trimethoxysilane, $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2$ (AEAP-TMS), which contains two amino groups, and 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane, $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ (AEAEAPTMS) which contains three amino groups. 3-Aminopropyltrimethoxysilane (AP-TMS), [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAP-TMS), and 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEAEAP-TMS) were purchased from Aldrich. Hexadecyltrimethylammonium chloride (C_{16} TMACl) and tetramethoxysilane (TMOS) were purchased from Tokyo Kasei. Monodispersed silica spheres (500 nm in diameter) were purchased from Nippon Shokubai Co., Ltd. All of the chemicals were used as-received. Hereinafter in this paper, we abbreviate the synthesized materials as MS-XY (where *X* is AP, AEAP or AEAEAP, and *Y* is 5%, 10% or 20%). *X* denotes the type of organic alkoxysilane that was used and *Y* denotes the molar ratio of R-TMS in the total silane monomer used in the co-condensation reaction. The co-condensation ratio (*Y*) is expressed as R-TMS/(TMOS + R-TMS), which was calculated by the added amount of silanes for the syntheses. In case of MS-AP5% with different particle diameter, we abbreviate the synthesized material as MS-AP5%-Z. *Z* denotes the particle diameter (310–780 nm).

The synthesis reactions were carried out under basic conditions, as follows.

For example, in the case of MS-AP5%, 3.52 g of C_{16} TMACl and 2.28 ml of 1 M sodium hydroxide solution were dissolved in 800 g of a methanol/water (50/50, w/w) solution (methanol ratio: 0.5). A mixture of 1.25 g (8.24 mmol) of TMOS and 0.08 g (0.43 mmol) of AP-TMS (AP-TMS/(TMOS + AP-TMS) = 5 mol%) were then added to the solution with vigorous stirring at 298 K. After the addition of the TMOS and the AP-TMS, the clear solution suddenly turned opaque and resulted in a white precipitate.

In the case of MS-AP5%-680 nm, the same amount of TMOS/AP-TMS mixture was again added to the solution 0.5 h later. 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 heated in 60 ml of ethanol solution containing 1 ml of concentrated hydrochloric acid (0.6 ml) at 333 K for 3 h to remove the templates. Then, the powder was filtered, washed several times with ethanol, and dried at 318 K.

The incorporation of an AP group into spherical silica that did not have mesopores was processed as follows: 1 g of monodispersed silica spheres were added to a mixture of 20 ml of dehydrated toluene and 0.2 g of AP-TMS, and the solution was then refluxed for 15 h at 363 K. The product was dried overnight at 318 K after filtration. The spherical silica on which a 3-aminopropyl group was covalently attached (SS-AP) was obtained.

2.2. Sample characterization

Powder X-ray diffraction measurements were carried out with a Rigaku Rint-2200 X-ray diffractometer using Cu-K α radiation. Scanning electron micrographs (SEMs) were obtained with 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 particle diameter distribution was judged. The nitrogen adsorption isotherm was measured using a Belsorp-mini II (BEL Japan) at 77 K. The sample was evacuated at 373 K under 10^{-3} mmHg before measurement. The pore diameter was calculated by using the Barrett–Joyner–Halenda (BJH) method. By considering the linearity of a Brunauer–Emmett–Teller (BET) plot, the specific surface area was 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 with a repetition delay of 2 s, 2 ms contact time, and 2.8 μs ^1H 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 varioEL elemental analyzer.

2.3. Catalytic reactions

Before the reaction, the amino-functionalized materials were treated with an ammonia solution to remove any residual Cl^- ions and to neutralize the protonated amines in the sample [24]. 0.35 g of the modified sample was suspended in 20 ml of a methanol solution containing 1 ml of ammonia solution (28%) at room temperature for 8 h. The solid was recovered by filtration, washed with ethanol, and finally dried in a vacuum at 423 K for 12 h.

The reactions were carried out in a round-bottomed flask equipped with a reflux condenser and were stirred magnetically. The nitroaldol condensation was typically carried out as follows: a reaction mixture consisting of 50 mg of the catalyst, 0.61 g (5.0 mmol) of *p*-hydroxybenzaldehyde in 10 ml of nitromethane, was heated at 363 K with constant stirring for 1 h. The mixture

was filtered and the catalyst was washed thoroughly with chloroform. The filtrate was evaporated under reduced pressure. The solid that was obtained was dissolved completely in a sufficient amount of acetone- d_6 . An internal standard, THF (≈ 10 mmol), was added into the acetone- d_6 solution. The product was analyzed by studying its ^1H NMR spectra on a JEOL JNM-LA500 NMR spectrometer [23].

In case when *p*-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.

3. Results and discussion

3.1. Synthesis of amino-functionalized MMSS

The morphology of the amino-functionalized mesoporous silica was observed using an SEM. SEM images are shown in Fig. 1. Table 1 presents the precipitation times of the particles (time precipitates appear after the addition of silica source), their average diameters and standard deviations as obtained from the SEM images. We consider particles with a standard deviation of below 10% to be monodispersed. Although the degree of monodispersity decreased with increasing number of amino groups in the molecule, monodispersed silica spheres were obtained for AP-TMS or AEAP-TMS with less than 10% of amine silica source added, or for AEAEAP-TMS with less than 5%. The reason for the decrease in monodispersity with increasing number of amino moieties was assumed to be because the uniformity of the reaction decreased due to the promoted condensation of silanol groups rather than the increased basicity of the reaction solution. The average diameters of the particles that were obtained were about 500–600 nm. The diameter of the particles decreased with increasing the amount of amino groups.

The degree of mesoporosity in the obtained silica was evaluated by powder XRD analysis. Fig. 2 shows the XRD patterns of samples synthesized under different AP-TMS ratios. From the lowered peak intensity, it was deduced that the degree of mesoporosity had decreased with increasing AP-TMS co-condensation ratio, although d_{100} peaks corresponding to hexagonal arrays of mesopores were observed for all of the particles. The decrease is due to the destruction of the regularity of arrays of micelles by the amino groups. A similar tendency was reported for MCM-41 [25] and SBA-15 [6], in which the AP groups were modified. In the case of MS-AP5%, a slightly higher peak was observed, indicating a higher degree of mesoporosity. Table 2 shows an analysis of samples with standard deviations of less than 10% in their XRD patterns, nitrogen adsorption measurements and nitrogen content. The intensity of d_{100} , which is an indicator of the degree of mesoporosity, tends to decrease with increasing concentration and number of incorporated amino moieties in the molecule. However, it was confirmed that all of the particles possessed hexagonal mesopores.

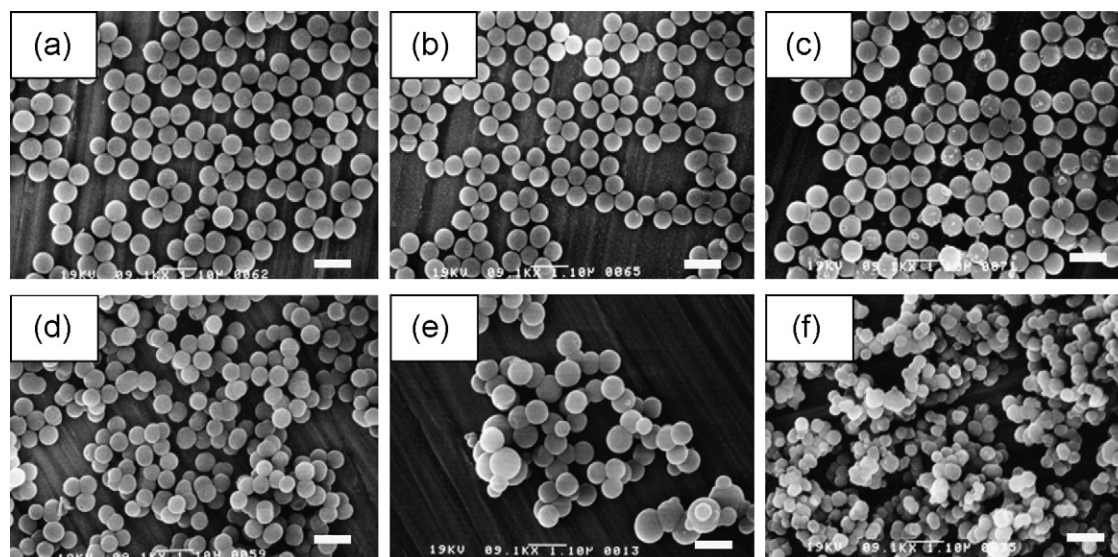


Fig. 1. Scanning electron micrographs of (a) MS-AP5%, (b) MS-AEAP5%, (c) MS-AEAEAP5%, (d) MS-AP20%, (e) MS-AEAP20%, and (f) MS-AEAEAP20%. Scale bar represents 1.1 μm .

Table 1
Properties of particles obtained from various silica precursors

Sample	R-TMS	Ratio of R-TMS (%)	Precipitation time ^a (s)	Average diameter (nm)	Standard deviation (%)
MS-AP5%	AP-TMS	5	145	600	5.3
MS-AP10%	AP-TMS	10	140	620	4.9
MS-AP20%	AP-TMS	20	130	550	14
MS-AEAP5%	AEAP-TMS	5	150	600	5.7
MS-AEAP10%	AEAP-TMS	10	150	540	6.1
MS-AEAP20%	AEAP-TMS	20	150	430	25
MS-AEAEAP5%	AEAEAP-TMS	5	150	560	10
MS-AEAEAP10%	AEAEAP-TMS	10	140	450	27
MS-AEAEAP20%	AEAEAP-TMS	20	135	340	31
MMSS	–	–	150	520	7.0

^a Time precipitates appear after the addition of TMOS and R-TMS.

The nitrogen adsorption–desorption isotherms were then measured and the distributions of the pores were analyzed by the BJH method. Fig. 3 shows the results for samples synthesized under different AP-TMS co-condensation ratios. The isotherms are type IV that is similar to the samples without any organic functional groups (MMSS). The pore volume decreased as the co-condensation ratio of the organic trimethoxysilane increased, and for MS-AP20%, almost no nitrogen was adsorbed. The other products (MS-AEAP, MS-AEAEAP) that were synthe-

sized using different organic silanes showed a similar tendency (Table 2). Among synthesized particles that were formed using R-TMS with the same co-condensation ratio, AP-TMS, which possess the smallest organic functional group, showed the largest pore size, specific surface area, and pore volume. It is considered that organic functional groups are incorporated into the pores. It can be seen from Table 2, MS-AP5%, MS-AP10% and MS-AEAP5% have highly ordered hexagonal regularity (intensity of $d_{100} > 10,000$) and large pore volumes (>0.4 ml/g).

Table 2
Structural properties of the amino-functionalized MMSS

Sample	XRD		Nitrogen Adsorption			N content (mmol/g)	
	d_{100} (nm)	Intensity (cps)	Pore size (nm)	S_{BET} (m^2/g)	Pore volume (ml/g)	Theoretical ^a	Experimental
MS-AP5%	3.56	12,600	1.96	930	0.52	0.77	0.49
MS-AP10%	3.69	10,400	1.91	790	0.44	1.54	0.68
MS-AEAP5%	3.63	12,500	1.79	800	0.42	1.45	0.73
MS-AEAP10%	3.52	4,600	1.62	480	0.22	1.90	1.57
MS-AEAEAP5%	3.80	6,600	1.77	650	0.34	2.04	1.27
MMSS	3.53	14,500	2.20	1090	0.76	–	–
SS-AP	–	–	–	4	–	–	0.12

^a Calculated from the amount used in the synthesis.

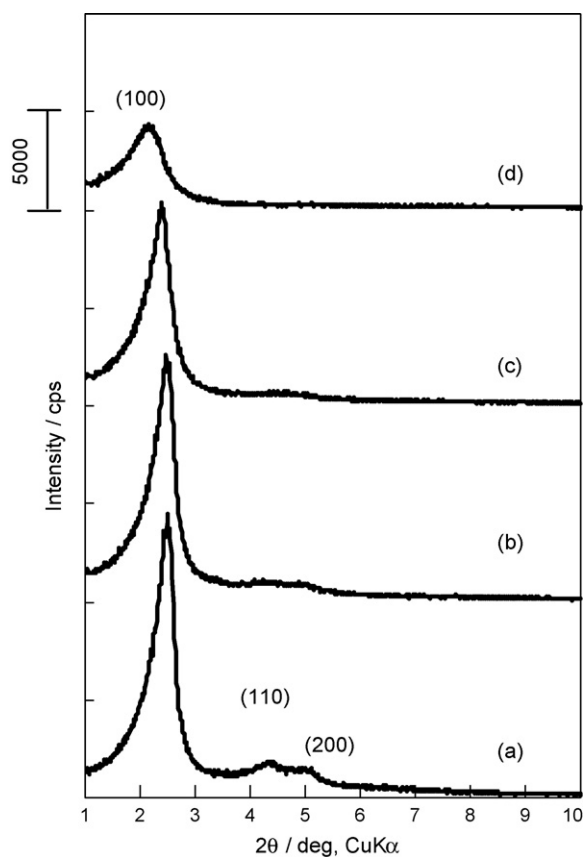


Fig. 2. XRD patterns of the samples obtained from different AP-TMS ratio: (a) MMSS, (b) MS-AP5%, (c) MS-AP10%, and (d) MS-AP20%.

The N contents of the samples were analyzed. Table 2 shows the measured values as well as calculated values from the amounts used in the syntheses. When the ratio for the organic functional groups in the synthesis (=R-TMS co-condensation ratio) was 5%, 64% (0.49/0.77) of the AP-TMS group, 50% (0.73/1.45) of the AEAP-TMS group and 62% (1.27/2.04) of the AEAEAP-TMS group were incorporated. In the case where the AP-TMS co-condensation ratio increased to 10%, the value decreased to 44%.

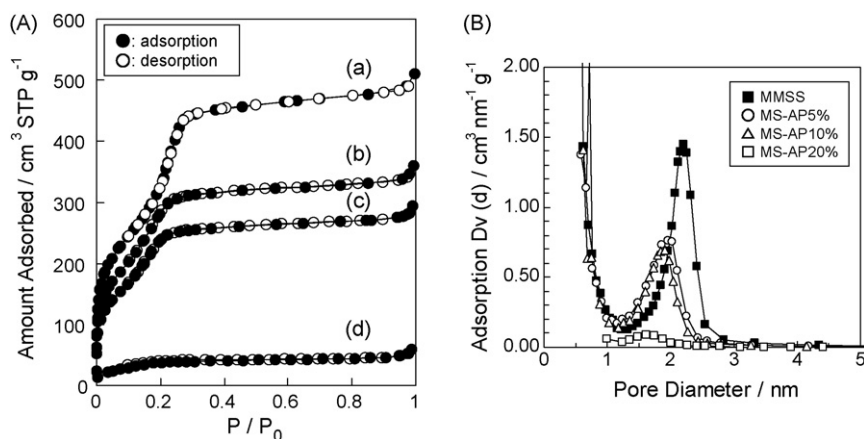


Fig. 3. (A) Nitrogen adsorption–desorption isotherms of (a) MMSS, (b) MS-AP5%, (c) MS-AP10%, (d) MS-AP20%, and (B) BJH pore size distributions of corresponding samples.

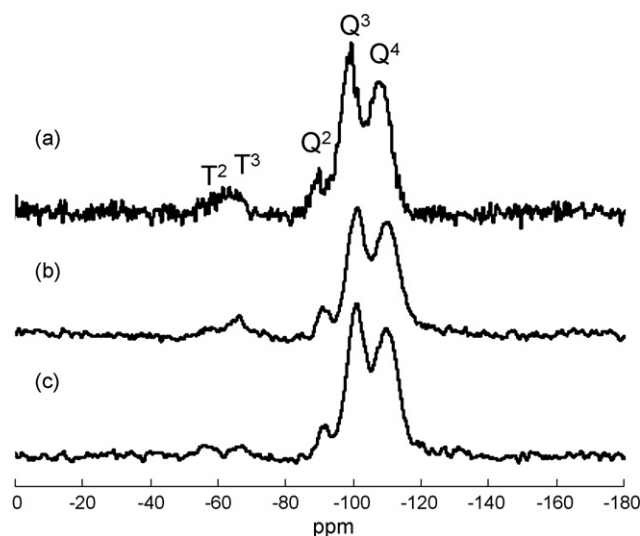


Fig. 4. ²⁹Si MAS NMR spectra of amino-functionalized MMSS: (a) MS-AP10%, (b) MS-AEAP10%, and (c) MS-AEAEAP5%.

Solid-state NMR analyses of MS-AP10%, MS-AEAP10%, and MS-AEAEAP5% were performed and their chemical structures were investigated. Fig. 4 shows the ²⁹Si MAS NMR spectra. Three clear resonance peaks derived from Qⁿ (Qⁿ = Si(OSi)_n(OH)_{4-n}, n = 2–4, Q⁴: δ = -110 ppm, Q³: δ = -100 ppm, Q²: δ = -90 ppm) and two peaks derived from T^m (T^m = RSi(OSi)_m(OH)_{3-m}, m = 1–3, T³: δ = -65 ppm, T²: δ = -55 ppm) were observed. The presence of the T^m peaks indicates the introduction of an organic functional moiety into the silica skeleton. Due to the small quantity of AEAEAP, the peaks for T³ and T² were not significant in the MS-AEAP5% if compared with the other samples. Fig. 5 shows the results of ¹³C CP MAS NMR analysis. All of the samples exhibited peaks derived from the C atoms of the combined organically functionalized groups. Furthermore, a peak derived from the ethoxy group was also observed, which indicates a partial esterification of silanol with ethanol, the solvent that was used for the extraction of templates.

Table 3
Properties of MS-AP5% with various diameter

Sample	Methanol ratio	Amount of Si source added (10^{-3} mol)	Average diameter (nm)	S.D. ^a (%)	d_{100} (nm)	Pore size (nm)	S_{BET} (m^2/g)	Pore volume (ml/g)	N content (mmol/g)
MS-AP5%-310 nm	0.45	–	310	7.2	3.89	2.38	920	0.70	0.49
MS-AP5%-490 nm	0.48	–	490	6.9	3.69	2.14	1060	0.72	0.49
MS-AP5%-680 nm	0.5	8.67	680	4.7	3.71	2.27	1060	0.77	0.56
MS-AP5%-780 nm	0.5	17.3	780	3.6	3.62	2.12	1020	0.67	0.55

^a Standard deviation.

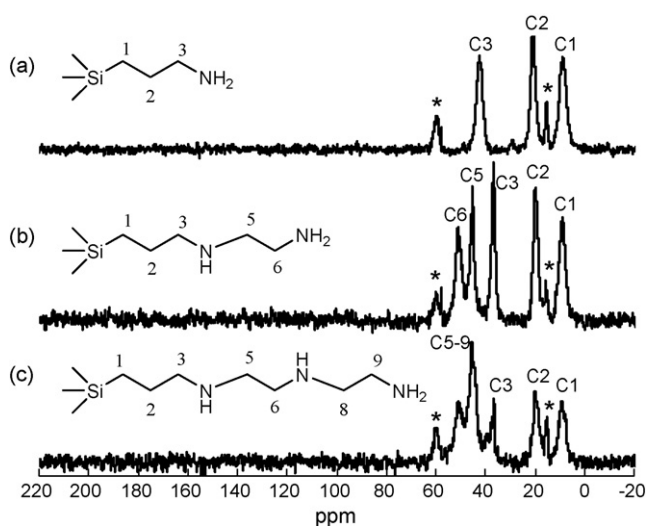


Fig. 5. ^{13}C CP MAS NMR spectra of amino-functionalized MMSS: (a) MS-API10%, (b) MS-AEAP10%, and (c) MS-AEAEAP5%. *Signals of residual ethoxy group.

The syntheses of MS-AP5% particles with different particle diameters were then investigated. The particle diameter was controlled by changing the methanol/water ratio or by adding extra silica source with a fixed co-polymerization ratio of 5%. Fig. 6 shows the SEM images and Table 3 shows the properties of the synthesized silica particles. It was revealed that the particle diameter can be decreased while retaining their monodispersity by decreasing the methanol/water ratio during the synthesis, and that is similar to the samples without any organic functional groups [23]. An average diameter of 310 nm for MS-AP5% was obtained by synthesis using a methanol ratio of 0.45. This is due to a decrease in the solubility of silica, meaning that the particles were precipitated more easily. By adding more of the silica source, particle diameter could be enlarged [26]. When the amount of added silica was equal to the original amount of silica, the diameter of the obtained monodispersed spherical particles was 680 nm (MS-AP5%-680 nm). On the contrary, when a twofold amount of silica was added, the diameter became 780 nm (MS-AP5%-780 nm). These particles, with diameters in the range between 310 nm and 780 nm, were all confirmed as possessing ordered mesopores and high specific surface areas of $1000 m^2/g$ by XRD analysis and by nitrogen absorption measurements, respectively. Fig. 7 shows a TEM

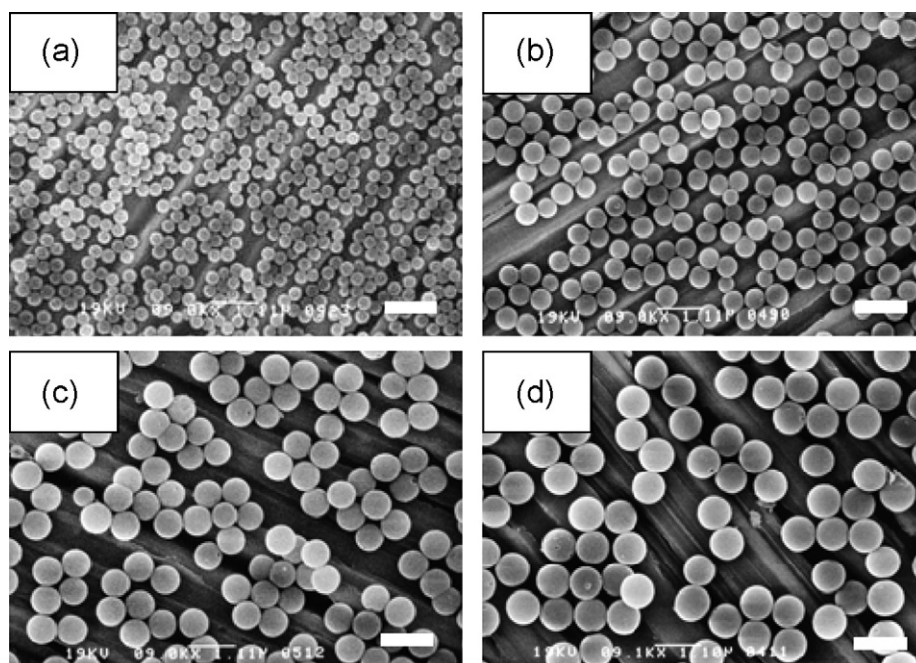


Fig. 6. Scanning electron micrographs of various size of MS-AP5%: (a) 310 nm, (b) 490 nm, (c) 680 nm, and (d) 780 nm. Scale bar represents $1.1 \mu m$.

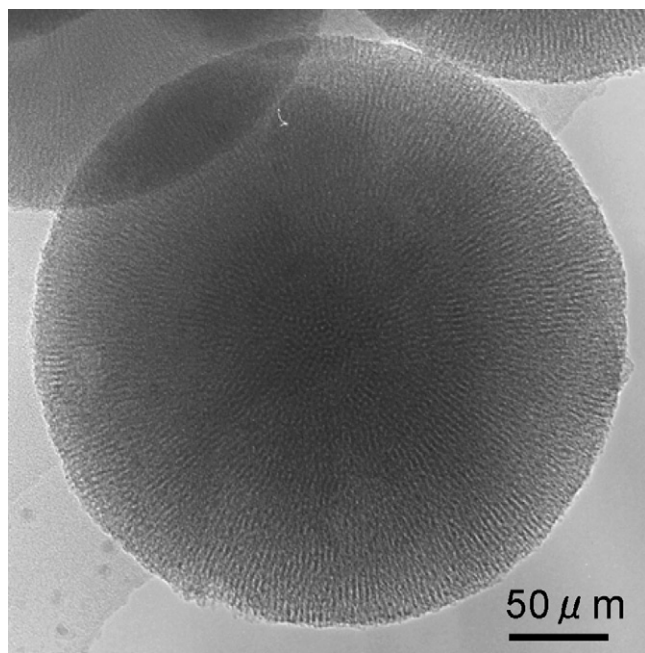


Fig. 7. Transmission electron micrograph of MS-AP5% with particle diameter of 310 nm.

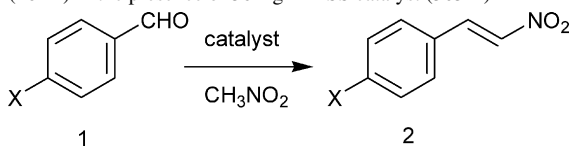
image of MS-AP5%-310 nm. Since the previously synthesized MMSS (which consisted of inorganic components alone) had particle diameters of 500 nm, an electron beam could not reach its core. Therefore, observation of its internal structure by TEM was conducted with metals introduced into the pores [21,22] or by cutting epoxy-resin-embedded MMSS by electron beam [26]. And it was revealed that hexagonally packed mesopores were aligned radially from the center to the surface of the MMSS. However, direct observation is possible for this size of particles (310 nm). As a result, it was observed that the hexagonal pores were arrayed in a radial pattern, as was observed for non-functionalized MMSS. This was the first direct observation of the radially aligned mesoporous structure of amino-functionalized mesoporous material.

3.2. Evaluation of basic catalytic activity for various MMSS

Various synthesized amino-functionalized MMSS were evaluated for their base catalytic performance by the nitroaldol condensation reaction of nitromethane and *p*-hydroxybenzaldehyde. Table 4 shows the results of the catalytic reactions. For comparison, the experimental results for spherical silica without pores grafted with an aminopropyl moiety (SS-AP) and a similar result that was reported in a literature 19 for non-monodispersed spherical mesoporous silica, in which AEAP is incorporated (MSN catalyst) are shown. MMSS that is not amino-functionalized shows no catalytic activity (Entry 9); however, amino-functionalized MMSS exhibits excellent catalytic activity. In the case of MS-AP5%, which possesses an aminopropyl group, the yield increased with increasing reaction time. When the reaction time increased from 1 h to 2 h, the yield increased from 82% to 94%, and the TON (turnover number) improved from 167 to 192 (Entries 2 and 3). Furthermore,

Table 4

Results of nitroaldol reactions of benzaldehyde (5 mmol) with nitromethane (10 ml) in the presence of 50 mg MMSS catalyst (363 K)



X = OH, NO₂

Entry	Catalyst	X	Time (h)	Yield (%)	TON ^a
1	MS-AP5%	OH	0.5	44	89
2	MS-AP5%	OH	1	82	167
3	MS-AP5%	OH	2	94	192
4	MS-AP10%	OH	1	91	134
5	MS-AEAP5%	OH	1	83	227
6	MS-AEAP10%	OH	1	14	18
7	MS-AEAEAP5%	OH	1	60	142
8	SS-AP	OH	1	7	58
9	MMSS	OH	1	0	0
10	MS-AP5% ^b	NO ₂	1	80	245
11	MS-AP5% ^b	NO ₂	3	100	306
12	MS-AEAP5% ^b	NO ₂	1	100	205
13	MSN catalyst (AEAEAP1.0 mmol/g) ^{b,c}	NO ₂	20	93	56

^a Turnover number = mmol product/mmol organic groups during reaction time.

^b Reaction conditions: 3 mmol of 4-nitrobenzaldehyde, 10 ml of nitromethane, 20 mg catalyst.

^c Data are from Ref. [19].

we make a comparison between MS-AP5% and MS-AP10%, then MS-AP10% exhibits higher yield (Entries 2 and 4) while MMSS-AP5% shows a value of TON that is 1.3 times higher. From this data, it was concluded that an optimum amount of amino groups exists for catalytic activity.

Comparative studies of reactions lasting for 1 h revealed that MS-AEAP5%, which contains two amino groups as catalytic sites in each molecule, shows the highest catalyst activity (TON: 227, Entry 5). However, when this is converted to “activity per amino-group” within the molecule, the equivalent value of TON is about 113, meaning that the individual activities of the amino groups are lower than for the cases of MS-AP5% (Entry 2) and MS-AP10% (Entry 4). Furthermore, MS-AEAP10% exhibited significantly lowered activity, in that the yield was 14% and TON was 18, even with the increase in the number of amino groups. This arises because of the decreased pore diameter (from 1.79 to 1.62 nm) with the increased volume of the AEAP group; thus, the diffusion rate of the reactant in the mesopores decreased.

In addition, MS-AEAEAP5% modified by AEAEAP (which has three amino groups) exhibited a TON of 142 (Entry 7), which equates to about 47 per amino group. When comparing Entries 2, 5, and 7, it was suggested that, with increasing number of amino groups in each organosilane, the relative value of TON decreases. The reason for this is that due to the incorporation of bulky molecules, the diffusion of *p*-hydroxybenzaldehyde (which is a nearby reactant of the reaction site) was interrupted. However, because there is a report that the efficiency of catalytic activity is in the order of primary amine > secondary

amine > tertiary amine [9], a relative comparison of TON by considering converted values per amino group might not be totally appropriate.

Amino-functionalized SS-AP obtained from non-porous spherical silica with a particle diameter of 550 nm (standard deviation 4.4%) by grafting AP-TMS showed a yield of 7% and a TON value of 58 (Entry 8). Therefore, the amino groups that are bound to the surfaces of the particles do possess some activity; however, due to their low specific surface area, the yield seems to be extremely low. As the result, it was considered that most of the catalytic reactions occur inside the pores.

Lin et al. reported on spherical mesoporous silica that incorporated AEAEAP (MSN catalyst: specific surface of 805.8 m²/g, pore volume 0.57 ml/g) [17] and its base catalytic activity [19]. They used *p*-nitrobenzaldehyde for the reactant and evaluated the catalytic reaction at 363 K for 20 h. The results showed that the yield was 93% and the value of TON was 56 (Entry 13). As a result of the evaluation under the same condition, MS-AP5% exhibited excellent activity, the yield was 80% and TON was 245 for 1 h (Entry 10). When the reaction time increased to 3 h, the yield reached to 100% (TON: 306, Entry 11). Surprisingly, MS-AEAP5% shows 100% yield in spite of the reaction time of 1 h (Entry 12). The MSN catalyst that was synthesized did not contain radially arrayed mesopores; thus, the diffusion of the reactants and the products could be limited. On the other hand, in the case of MMSS particles that have radially arrayed mesopores, the diffusion of reactants and products occurs easily, indicating that their use as a catalyst is advantageous.

3.3. Effect of particle diameters on catalytic activity

An evaluation of base catalytic reactions was performed using AP-modified MMSS which had different particle diameters but almost the same pore size. The co-condensation ratio of AP-TMS was always 5 mol%. The results are shown in Table 5. The results revealed that catalytic activity dependent on the particle diameters when they are in the range between 490 nm and 780 nm, and that the smaller the diameter, the higher the activity. This is because most of the surfaces of the particles consist of mesopores, then the smaller the particle, the greater the number of pores that are accessible per unit weight. However, the activity actually decreased for the smallest diameter of particle, MS-AP5%-310 nm. This happened because, with the smaller diameter, the aggregation of particles becomes a significant fac-

Table 5

Results of nitroaldol reactions of 4-hydroxybenzaldehyde (5 mmol) with nitromethane (10 ml) in the presence of 50 mg MMSS catalyst (363 K, 1 h)

Entry	Catalyst	Yield (%)	TON ^a
1	MS-AP5%-310 nm	70	137
2	MS-AP5%-310 nm ^b	80	164
3	MS-AP5%-490 nm	82	167
4	MS-AP5%-680 nm	86	152
5	MS-AP5%-780 nm	75	135
6	MS-AP5%-780 nm ^b	75	135

^a Turnover number = mmol product/mmol organic groups per reaction time.

^b Sonication was applied for 1 h before the reaction.

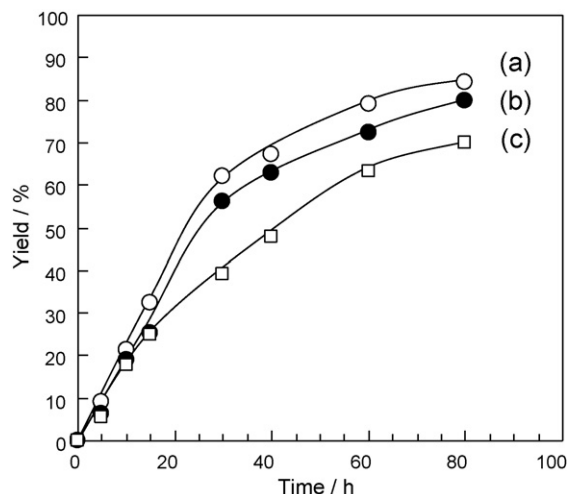


Fig. 8. Changes in the activity of MMSS catalyst having different particle diameter in nitroaldolcondensation reaction: (a) MS-AP5%-490 nm, (b) MS-AP5%-680 nm, and (c) MS-AP5%-780 nm.

tor. Therefore, sonication was performed prior to the reaction in order to prevent aggregation. As a result, the activity recovers to the same level as that of MS-AP5%-490 nm. The catalytic activity of MS-AP5%-780 nm exhibited the same levels with or without sonication. These results lead to the conclusion that particles tend to aggregate as their diameters decrease and that catalytic activity decreases for particles of 310 nm.

In order to investigate what ratio of mesopores were effectively used for a catalytic reaction, the effectiveness factor (η) was estimated. We used *p*-methoxybenzaldehyde as the reactant to compare the effectiveness factor of this system with amino-functionalized MMSS prepared by grafting method [23]. Fig. 8 shows time course of yields of nitroaldol condensation of nitromethane and 4-methoxybenzaldehyde using MS-AP5%-490 nm, MS-AP5%-680 nm, and MS-AP5%-780 nm as a catalyst. Table 6 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 catalysts. Initial rates determined from data at the reaction time of 10 min for MS-AP5%-490 nm, MS-AP5%-680 nm, and MS-AP5%-780 nm were 2.1, 1.9, and

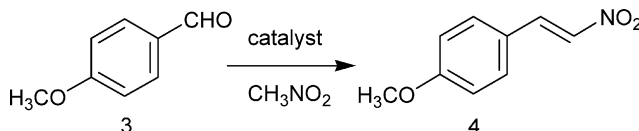
Table 6

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 (min ⁻¹) ^a	TON ^b (yield %)
MS-AP5%-490 nm	2.1	4.3	161 (79)
MS-AP5%-680 nm	1.9	3.4	129 (72)
MS-AP5%-780 nm	1.8	3.2	115 (63)

^a Turnover frequency = mmol product/mmol organic groups during initial 10 min.

^b Turnover number = mmol product/mmol organic groups during 1 h.



1.8 mmol g_{cat}⁻¹ min⁻¹, respectively. From these rates and particle diameters data, the effectiveness factor of MMSS was evaluated to be in the range between 0.80 and 0.82. The effective factor of the amino-functionalized MMSS prepared by grafting method was 0.63 and it was found that the effective factor of MMSS prepared by co-condensation method (MS-AP samples) increases greatly. Because both samples have almost the same properties (except for their preparation methods), it is considered that the distribution of organic functional group was affected by the synthesis method. The grafting method is said to be difficult to incorporate organic functional groups into mesopores homogeneously, and leads to higher concentration of organic functional groups near the pore windows [15]. On the contrary, organic functional groups were incorporated homogeneously into MS-AP samples prepared by co-condensation method and MS-AP samples have turned out to be excellent catalysts. Thus, these are significant and effective materials for use in fundamental studies of catalytic reactions.

4. Conclusions

The synthesis of amino-functionalized monodispersed mesoporous silica spheres with ordered hexagonal regularity was achieved for the first time using co-condensation reactions. TEM observations revealed that the mesopores were aligned radially from the center towards the outside of the spheres. By changing the conditions for the synthesis or adding extra silica source, amino-functionalized MMSS with almost the same pore size and different particle diameters were successfully synthesized. Evaluations of the base catalytic activity of these particles confirm their effectiveness in catalysis due to their radially aligned mesopores. The effectiveness factor of the particles improved greatly when compared with other types of amino-functionalized MMSS catalysts prepared by grafting method. Furthermore, because these materials possess identical particle diameters, they can be useful as ideal materials for the fundamental study of catalysis.

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References

- [1] A.P. Wight, M.E. Davis, *Chem. Rev.* 102 (2002) 3589.
- [2] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem. Int. Ed.* 45 (2006) 3216.
- [3] E. Angeletti, C. Canepa, G. Martinetti, P. Venturello, *Tetrahedron Lett.* 29 (1988) 2261.
- [4] D.J. Macquarrie, D.B. Jackson, *Chem. Commun.* (1997) 1781.
- [5] Y. Kubota, Y. Nishizaki, H. Ikeya, M. Saeki, T. Hida, S. Kawazu, M. Yoshida, H. Fujii, Y. Sugi, *Micropor. Mesopor. Mater.* 70 (2004) 135.
- [6] X.G. Wang, K.S.K. Lin, J.C.C. Chan, S.F. Cheng, *J. Phys. Chem. B* 109 (2005) 1763.
- [7] F. Bigi, S. Carloni, R. Maggi, A. Mazzacani, G. Sartori, *Stud. Surf. Sci. Catal.* 130 (2000) 3501.
- [8] G. Demicheli, R. Maggi, A. Mazzacani, P. Righi, G. Sartori, F. Bigi, *Tetrahedron Lett.* 42 (2001) 2401.
- [9] Y. Kubota, K. Goto, S. Miyata, Y. Goto, Y. Fukushima, Y. Sugi, *Chem. Lett.* 32 (2003) 234.
- [10] Y. Kubota, H. Ikeya, Y. Sugi, T. Yamada, T. Tatsumi, *J. Mol. Catal. A* 249 (2006) 181.
- [11] A.C. Blanc, D.J. Macquarrie, S. Valle, G. Renard, C.R. Quinn, D. Brunel, *Green Chem.* 2 (2000) 283.
- [12] X.G. Wang, Y.H. Tseng, J.C.C. Chan, S.F. Cheng, *J. Catal.* 233 (2005) 266.
- [13] M. Luechinger, A. Kienhöfer, G.D. Pirngruber, *Chem. Mater.* 18 (2006) 1330.
- [14] S. Shylesh, A.R. Singh, *J. Catal.* 244 (2006) 52.
- [15] H. Yoshitake, *New J. Chem.* 29 (2005) 1107.
- [16] S. Sadasivan, D. Khushalani, S. Mann, *J. Mater. Chem.* 13 (2003) 1023.
- [17] S. Huh, J.W. Wiench, J.C. Yoo, M. Pruski, V.S.Y. Lin, *Chem. Mater.* 15 (2003) 4247.
- [18] S. Huh, H.T. Chen, J.W. Wiench, M. Pruski, V.S.Y. Lin, *J. Am. Chem. Soc.* 126 (2004) 1010.
- [19] S. Huh, H.T. Chen, J.W. Wiench, M. Pruski, V.S.Y. Lin, *Angew. Chem. Int. Ed.* 44 (2005) 1826.
- [20] K. Yano, Y. Fukushima, *Bull. Chem. Soc. Jpn.* 75 (2002) 1977.
- [21] K. Yano, Y. Fukushima, *J. Mater. Chem.* 13 (2003) 2577.
- [22] K. Yano, Y. Fukushima, *J. Mater. Chem.* 14 (2004) 1579.
- [23] T.M. Suzuki, M. Yamamoto, K. Fukumoto, Y. Akimoto, K. Yano, *J. Catal.* 251 (2007) 249.
- [24] T. Yokoi, H. Yoshitake, T. Yamada, Y. Kubota, T. Tatsumi, *J. Mater. Chem.* 16 (2006) 1125.
- [25] T. Yokoi, H. Yoshitake, T. Tatsumi, *J. Mater. Chem.* 14 (2004) 951.
- [26] T. Nakamura, M. Mizutani, H. Nozaki, N. Suzuki, K. Yano, *J. Phys. Chem. C* 111 (2007) 1093.