

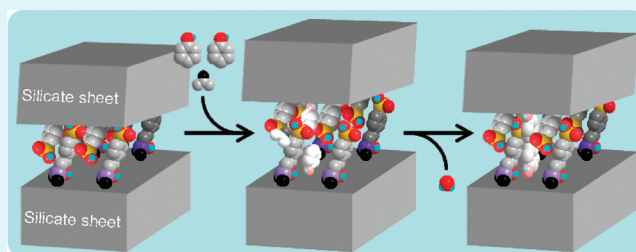
Effective and Selective Bisphenol A Synthesis on a Layered Silicate with Spatially Arranged Sulfonic Acid

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ABSTRACT: The silylated derivatives of a layered alkali silicate, magadiite, modified with propylsulfonic or arylsulfonic acid were synthesized and used as catalysts for an acid-catalyzed condensation of phenol with acetone. The propylsulfonated magadiites with a different amount of the attached silyl group were synthesized by the silylation of the dodecylammonium-exchanged magadiite with the tuned amount of 3-(mercaptopropyl)trimethoxysilane and the subsequent oxidation of the attached thiol to sulfonic acid. The arylsulfonated magadiite was synthesized by the silylation of the dodecylammonium-exchanged magadiite with 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane and the subsequent hydrolysis of the attached sulfonyl chloride to sulfonic acid. The X-ray diffraction (XRD) patterns and elemental mappings of the products, and the photoluminescent spectra of the Eu³⁺-exchanged products suggested that propylsulfonic or arylsulfonic acid was homogeneously distributed in the interlayer space. When all the sulfonated materials were used as an acid catalyst for condensation between phenol and acetone, *p,p'* bisphenol A selectively formed over the *o,p'* isomer, and higher yield and selectivity were attained on the catalysts with larger amount of the attached sulfonic acid. When the interlayer space of the propylsulfonated magadiite was expanded by the co-attachment of octadecylsilyl group, lower selectivity was obtained. The arylsulfonated magadiite showed considerably higher *p,p'* bisphenol A yield than the propylsulfonated magadiites.

KEYWORDS: layered alkali silicate, magadiite, silylation, silane coupling reagent, sulfonic acid, thiol, solid acid catalyst, bisphenol A



INTRODUCTION

Materials that allow for molecular-level structural and compositional fine tuning have attracted increased attention to mimic enzyme reactions.^{1–4} Layered inorganic solids and the organic derivatives are the possible candidates due to the large surface area, which is derived from well-defined nanostructures composed of ultrathin oxide layers (so called “nanosheets”), materials diversity, and chemical stability if compared to organic counterparts.^{5–13} The organic derivatives with silane coupling reagents^{14–17} have exhibited unique molecular recognition abilities, possibly due to the controlled spatial distribution of one or multiple kinds of functional groups in the interlayer nanospace.^{16,18–28} These reports motivate us to design silylated layered materials toward stereo-, regio-, and chemoselective syntheses of target organic compounds.

In this article, we have newly synthesized the silylated derivatives of a layered silicate, magadiite,^{29–31} modified with alkylsulfonic or arylsulfonic acid, and investigated the catalytic activity of the sulfonated magadiites using bisphenol A synthesis as a model regioselective organic synthesis. Bisphenol A is an important industrial feedstock, especially as monomer in polycarbonate materials and epoxy resins. It has been synthesized by acid-catalyzed condensation between acetone and phenol, yielding the desired *p,p'* isomer and a by-product, the *o,p'* isomer. The addition of thiols as a co-catalyst is known to improve both the yield and the selectivity to the desired

isomer;³² accordingly, a lot of effort has been focused toward designing heterogeneous catalysts containing acids such as alkylsulfonic and arylsulfonic acids and thiols like alkylthiol to develop novel processes alternative to the existing processes such as those using sulfonated resins where poor thermal stability is a key limitation of these materials.^{33–39} In this study, the *p,p'* isomer effectively and extraordinarily selectively formed on the silylated magadiite modified only with arylsulfonic acid. The result was explained by the spatially arranged arylsulfonic acid that played an important role in positioning phenols so that the reactants preferentially condensed into *p,p'* bisphenol A. A wide variety of silane coupling reagents are available, and the surface coverage with one or multikinds of silyl groups on nanosheets is precisely tuned;^{18–27,40} therefore, the present result shows a first step for the production of a wide variety of target organic compounds on silylated layered materials.

EXPERIMENTAL SECTION

Materials and Reagents. Magadiite (Na₂Si₁₄O₂₉) was synthesized according to the reported method.⁴¹ 3-(Mercaptopropyl)-trimethoxysilane (MPS, 95.0 %), octadecyltrichlorosilane (C₁₈TMS, > 85.0 %), dodecyltrimethylammonium (C₁₂TMA) chloride (≥98.0 %), and tris(2-carboxyethyl)phosphine (TCEP) hydrochloride (≥98.0

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%) were purchased from Tokyo Chemical Industry Co., Ltd. A solution of 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPEs) in dichloromethane (50 %) was obtained from Gelest, Inc. Dehydrated toluene and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were obtained from Wako Pure Chemical Industries, Ltd. Phenol (99 %), and acetonitrile (99.8 %) and acetone (99 %) were purchased from Kanto Chemical Co., Inc. and Nacalai Tesque, Inc., respectively. All the reagents were used as received.

Synthesis of Sulfonated Magadiites. The grafting of sulfonic acid on solids surface has widely been investigated so far.^{42–46} In this study, the immobilization of propylsulfonic acid on magadiite was conducted on the basis of the procedure described in our previous report²² with slight modification. The C_{12}TMA -exchanged form of magadiite (named as C_{12}TMA -mag) (0.80 g), which was prepared by the reaction of magadiite with an aqueous solution of C_{12}TMA chloride,⁴⁷ was mixed with the tuned amount of MPS in de-hydrated toluene (80 mL) at 60 °C for 24 h, and the solvent was evaporated from the mixture. The precipitate was reacted with a solution of TCEP hydrochloride (TCEP/MPS = 2:1 in mole) in a mixed solution of water (20 mL) and ethanol (30 mL) at 50 °C for 2 days, to reduce disulfide to thiol, and the product was separated by filtration followed by washing with a mixture of ethanol (20 mL) and 1 mol L^{-1} of an aqueous HCl solution (20 mL). The resulting propylthiol-modified magadiite (named as PT_x -mag, x denotes the amount (groups) of the attached propylthiol per $\text{Si}_{14}\text{O}_{29}$) (0.20 g) was mixed with 7 mol L^{-1} of an aqueous H_2NO_3 solution (40 mL), and the mixture was stirred at room temperature for 6 h. This procedure was repeated to increase the amount of the attached sulfonic acid. The propylsulfonated product, named as PS_x -mag (x denotes the amount (groups) of the attached propylsulfonic acid per $\text{Si}_{14}\text{O}_{29}$), was separated by filtration, washed with 1 mol L^{-1} of an aqueous HCl solution, and then washed with water. Arylsulfonated magadiite was synthesized as follows: C_{12}TMA -mag (0.4 g) was mixed with 40 mL of a dichloromethane solution of CSPEs (50 %), and the mixture was stirred at room temperature. The product (AS_x -mag, x denotes the amount (groups) of the attached arylsulfonic acid per $\text{Si}_{14}\text{O}_{29}$) was separated by centrifugation (3500 rpm, 20 min), washed with 1 mol L^{-1} of an aqueous HCl solution, and finally washed with water. In order to synthesize the propylsulfonated magadiite where octadecyl groups was co-attached (abbreviated as $\text{PS}_x\text{-OD}_y$ -mag, where x and y are the amount (groups) of the attached propylsulfonic acid and octadecyl groups, respectively, per a $\text{Si}_{14}\text{O}_{29}$ unit cell), C_{12}TMA -mag was reacted with the tuned amount of C_{18}TMS and MPS sequentially, and the product was oxidized.

Synthesis of Bisphenol A. Catalyst (0.02 mmol of H^+) was added to vial (50 mL) and dried under vacuum at 60 °C for 6 h. Phenol (24 mmol) and acetone (6 mmol) were added; the vial was sealed under argon, and the mixture was stirred for 48 h. The reaction was conducted at 90 or 150 °C. The catalyst was removed by filtration and washed with acetonitrile to a total filtrate volume of 100 mL, and the filtrate was quantified by HPLC.

Characterizations. X-ray diffraction patterns of the solid products were collected using a powder X-ray diffractometer (Bruker D8 Advance) with graphite monochromatized $\text{Cu K}\alpha$ radiation at 40 kV and 30 mA. The crystal morphology was observed by scanning electron microscopy (SEM, Hitachi S-4800), and elemental mapping of products was conducted by SEM and energy-dispersive X-ray analysis. Thermogravimetric-differential thermal analysis (TG-DTA) curves were collected using a SSC/5200 apparatus (Seiko Instruments). The sample was heated from room temperature to 800 °C in an air flow (50 mL min^{-1}) at a rate of 10 °C min^{-1} . ^{13}C CP/MAS NMR and ^{29}Si MAS NMR spectra were recorded at 600 MHz on a Varian 600 spectrometer using a 6 mm-diameter zirconia rotor spinning at 5 kHz. The spectra were acquired using 4.8 μs 90° pulse length, 50 s recycle delay, and 1000 scans for ^{13}C CP/MAS NMR and 6.7 μs 90° pulse length, 100 s recycle delay, and 500 scans for ^{29}Si MAS NMR, respectively. The ^{13}C and ^{29}Si chemical shifts were referenced to hexamethylbenzene and 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt, respectively. Inductively coupled plasma-atopic emission spectroscopy (ICP-AES) was performed on a SPS 7700 plasma spectrometer (Seiko Instruments). Photoluminescent spectra were recorded on a Hitachi F-4500 fluorospectrophotometer

with an excitation wavelength of 394 nm. HPLC was performed on a Shimadzu 20A series instrument, and detection was carried out at 272 nm. The analysis was done with an isocratic method of a 60:40 H_2O /acetonitrile (0.01% trifluoroacetic acid) mixed solution using an ODS column (STR ODS-II, Shinwa Chemical Ind. Ltd.).

RESULTS AND DISCUSSION

Synthesis of Sulfonated Magadiites. The X-ray diffraction patterns of magadiite, C_{12}TMA -mag, $\text{PT}_{1.0}$ -mag, and $\text{PS}_{1.0}$ -mag are shown in Figure 1. The basal spacing (2.7

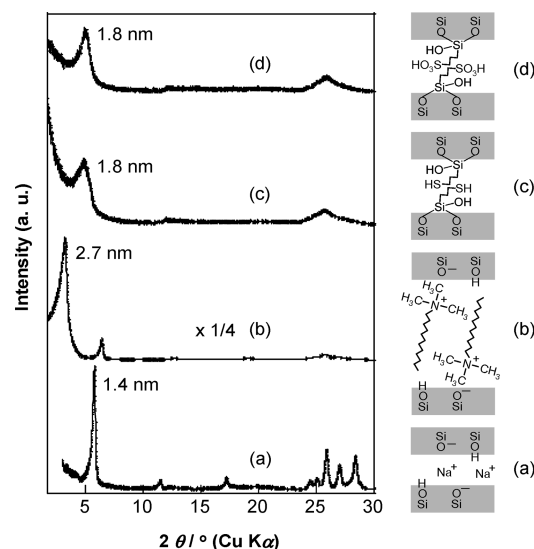


Figure 1. X-ray diffraction patterns of (a) magadiite, (b) C_{12}TMA -mag, (c) $\text{PT}_{1.0}$ -mag, and (d) $\text{PS}_{1.0}$ -mag. Inset shows the schematic structures of the corresponding samples.

nm) of C_{12}TMA -mag decreased to 1.8 nm after the silylation with MPS and did not change after the subsequent oxidation. In the ^{29}Si MAS NMR spectrum of $\text{PS}_{1.0}$ -mag, the integral ratio of Q^3/Q^4 , which reflects the amount of interlayer silanol groups, was substantially smaller than that of magadiite (Figure 2, left), indicating the covalent attachment of MPS on the silicate sheet via $\text{Si}-\text{O}-\text{Si}$ covalent bonds. The ^{13}C CP/MAS

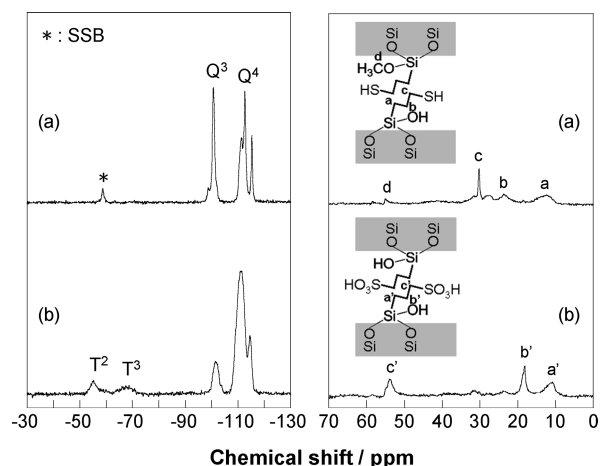


Figure 2. (left) ^{29}Si MAS NMR spectra of (a) magadiite and (b) $\text{PS}_{1.0}$ -mag and (right) ^{13}C CP/MAS NMR spectra of (a) $\text{PT}_{1.0}$ -mag and (b) $\text{PS}_{1.0}$ -mag. Inset shows the schematic nanostructures of the corresponding samples.

NMR spectra (Figure 2, right) and compositions (determined from TG curves and acid titrations, Table 1) of PS_{1.0}-mag

Table 1. Composition of Sulfonated Magadiites

	SiO ₂ /wt %	attached SO ₃ H ^a /groups per Si ₁₄ O ₂₉	adsorbed Eu(III) ^b /groups per Si ₁₄ O ₂₉
PS _{1.0} -mag	79	0.96	0.34
PS _{0.8} -mag	84	0.78	0.28
PS _{0.6} -mag	86	0.63	0.23
AS _{1.0} -mag	75	0.96	

^aDetermined by titration curves: the sulfonated material (5.0 mg) was mixed with an aqueous NaCl solution (2.0 mol L⁻¹, 40 mL), and the mixture was stirred for 1 day. The solid was removed by filtration, and then, the supernatant was titrated with a 0.01 mol L⁻¹ NaOH aqueous solution to obtain a titration curve. ^bPS_x-mag was added to an aqueous solution of EuCl₃·6H₂O (Eu/SO₃H = 1:1 in mole), and the mixture was stirred at room temperature for 1 day. After the product was separated by filtration, the concentration of the remaining Eu ions in the supernatant was determined by ICP-AES.

before and after oxidation revealed that the attached thiol was almost quantitatively converted to sulfonic acid. Similar results on X-ray diffraction (XRD) patterns, NMR spectra, and compositions were obtained when the amount of the added MPS was changed, indicating the formation of the silylated magadiites with the controlled amount of the attached propylsulfonic acid in the interlayer space (Table 1). As shown in Figure 2 (right, b), a slight amount of the remained thiol and the incompletely oxidized thiol like disulfide existed in PS_{1.0}-mag; however, these groups played a minor role in the present bisphenol A synthesis (see below).

We have characterized the spatial distribution of the attached silyl groups in the interlayer space of PS_x-mag. Figure 3 shows

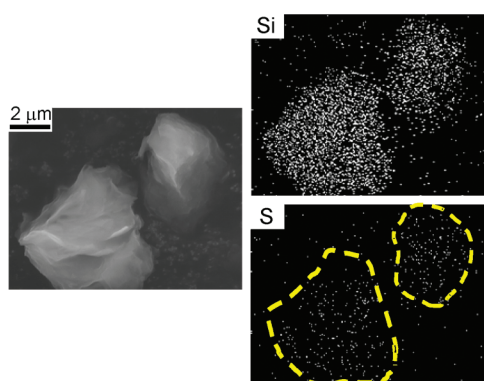


Figure 3. SEM image of PT_{1.0}-mag and the corresponding elemental mapping of a particle.

the elemental mapping of PT_{1.0}-mag (the particles of PS_x-mag were so aggregated that it was difficult to measure the elemental mapping of a particle; therefore, we used PT_x-mag for the measurement). S, which indicates the presence of the silyl group, was not concentrated on the edge of the particle but entirely distributed within the particle. Moreover, the XRD patterns of PS_x-mag were single phase (if the silyl groups are segregated, peaks due to the basal spacing should be split), and there was a linear relationship between the basal spacing and

the amount of the attached propylsulfonic acid (Figure 4). These results indicate the distance between the adjacent

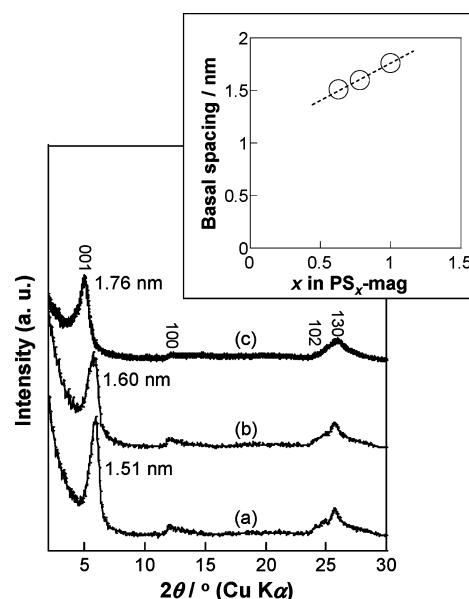


Figure 4. X-ray diffraction patterns of (a) PS_{0.6}-mag, (b) PS_{0.8}-mag, and (c) PS_{1.0}-mag. Inset shows the variation of basal spacing as a function of the amount of the attached propylsulfonic acid.

propylsulfonic acid groups varies systematically and strongly suggest propylsulfonic acid is homogeneously distributed on the silicate sheet.^{18–26,40}

The spatial distribution of the attached silyl group in PS_x-mag was further investigated using Eu³⁺ as a luminescent probe, since Eu³⁺ adsorbed almost quantitatively on PS_x-mag by cation exchange with H⁺ of the attached sulfonic acid (Table 1). In the photoluminescence spectra of the Eu³⁺-exchanged PS_x-mag (Figure 5), the luminescence bands ascribable to ⁵D₀-⁷F₁, ⁵D₀-⁷F₂, ⁵D₀-⁷F₃, and ⁵D₀-⁷F₄ transitions of Eu³⁺ were observed at 589, 611, 647, and 695 nm, respectively.^{48–51} The relative luminescence intensity ratio of each transition, which varies depending on the strength and symmetry of the electric field

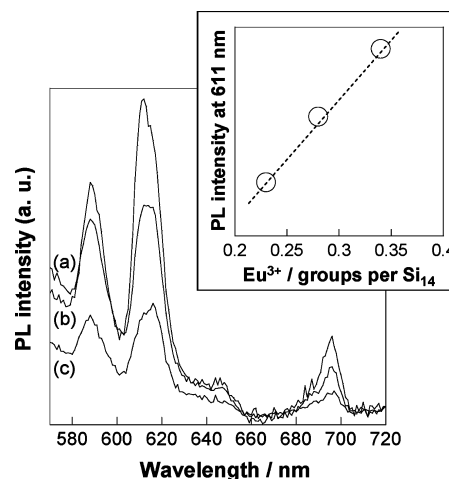


Figure 5. Photoluminescence spectra of Eu³⁺-exchanged PS_x-mag: (a) PS_{1.0}-mag, (b) PS_{0.8}-mag, and (c) PS_{0.6}-mag. Inset shows dependence of ⁵D₀-⁷F₁ photoluminescence intensity (611 nm) on Eu³⁺ concentration in PS_x-mag.

around Eu^{3+} , changed only slightly depending on the amount of the exchanged Eu^{3+} on $\text{PS}_x\text{-mag}$, showing that the Eu^{3+} ions adsorbed in a similar manner. As shown in Figure 5 inset, there was a linear relationship between the intensity of the ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ luminescence band and the adsorbed amount of Eu^{3+} . This observation is explained by the concentration quenching of Eu^{3+} ions that is suppressed by the spatial separation. The single layer of magadiite is so thick (ca. 1 nm) that it is difficult for Eu ions to interact across the silicate sheets.⁵¹ Therefore, the spatially isolated sulfonic acid in an interlayer space of magadiite possibly immobilizes Eu^{3+} to effectively suppress the luminescence self-quenching.

The attachment of arylsulfonic acid on magadiite was confirmed by the XRD pattern and ${}^{29}\text{Si}$ NMR and ${}^{13}\text{C}$ CP/MAS NMR spectra of the product. The basal spacing of $\text{C}_{12}\text{TMA-mag}$ (2.7 nm) decreased to 2.2 after the silylation with CSPES and the subsequent hydrolysis of the sulfonyl chloride (Figure 6, right). The ${}^{29}\text{Si}$ MAS NMR spectrum of the

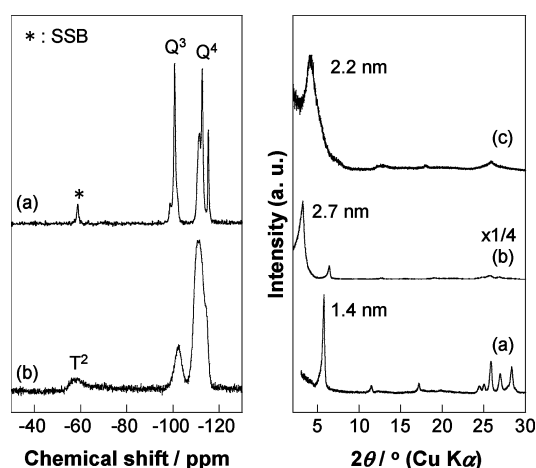


Figure 6. (left) ${}^{29}\text{Si}$ MAS NMR spectra of (a) magadiite and (b) $\text{AS}_{1.0}\text{-mag}$ and (right) XRD patterns of (a) magadiite, (b) $\text{C}_{12}\text{TMA-mag}$, and (c) $\text{AS}_{1.0}\text{-mag}$.

product indicated that the integral ratio of Q^3/Q^4 was considerably smaller than that of magadiite (Figure 6, left b) and the ${}^{13}\text{C}$ CP/MAS NMR spectrum showed no signals other than those due to *p*-ethylbenzenesulfonic acid group (data not shown). The amount of the attached arylsulfonic acid was determined by the titration to be 1.0 groups per $\text{Si}_{14}\text{O}_{29}$. Since the XRD pattern of $\text{AS}_{1.0}\text{-mag}$ showed that the product was single phase, it is suggested that arylsulfonic acid is

homogeneously distributed on the silicate sheets. Taking the size of the silyl groups and the single-layer thickness (ca. 1.0 nm) of magadiite into consideration, the observed basal spacing of all sulfonated materials is explained if propylsulfonic acid or arylsulfonic acid takes an interdigitated monolayer arrangement as schematically depicted in Figure 2 (inset of the right figure). T^2 signals were predominantly observed in the ${}^{29}\text{Si}$ MAS NMR spectra of the sulfonated magadiites, revealing the presence of hydroxy group in the attached silyl group which can interact with the hydroxy group of phenol (Figure 2, right inset). From all the results described above, we successfully synthesized the organic derivatives of magadiite with controlled spatial distribution of the attached propylsulfonic acid or arylsulfonic acid on the silicate sheets by changing the kind and the amount of the added silane coupling reagents (Table 1).

Bisphenol A Synthesis on Sulfonated Magadiites.

When all the propylsulfonated magadiites were reacted with acetone and phenol, products other than bisphenol A were hardly detected in HPLC and *pp'* bisphenol A was preferentially formed over the *o,p'* isomer (Table 2). The formation of bisphenol A resulted from sulfonic acid-catalyzed condensation between the reactants, since neither the proton-exchanged magadiite nor $\text{PT}_x\text{-mag}$, with no sulfonic acid, showed the activity toward the reaction (Nos. 1 and 2, Table 2). The yield and selectivity for *pp'* bisphenol A formation varied with temperature and the amount and the kind of the attached sulfonic acid. $\text{AS}_{1.0}\text{-mag}$ at 150 °C gave the best result with a yield of 49 TON and selectivity of 260 *pp'*/*o,p'* isomer ratio (No. 9, Table 2). The selectivity was considerably higher than those reported for other heterogeneous catalysts containing acids and thiols; for example, *pp'*/*o,p'* isomer ratios of 19 and 24 were attained over a mesoporous silica (SBA-15) modified with propylthiol and arylsulfonic acid³⁶ and a heteropolyacid ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$) modified with aminoethanethiol,³⁷ respectively. Also, the yield on $\text{AS}_{1.0}\text{-mag}$ (49 TON is equivalent to 1 TOF) was comparable to those reported for the previous studies. For example, propylthiol and arylsulfonic acid-modified SBA-15 showed 108 TON (4 TOF).³⁶

Higher yields were attained on the sulfonated materials with a larger amount of the attached silyl group. This was possibly due to larger gallery height, which made the reactants intercalate more efficiently. Also, the selectivity strongly depended on the amount of the attached silyl group. This result was explained by propyl (or phenylethyl) group and hydroxy group in the attached silyl group that cooperatively interacted with phenyl group and hydroxy group of phenol

Table 2. Results of Bisphenol A Formation on the Present Materials

no.	catalyst	temp./°C	$\text{SO}_3\text{H}/\text{mmol g}^{-1}$	basal spacing/nm	<i>pp'</i> yield/ mmol g^{-1} (TON) ^a	selectivity/ <i>pp'</i> / <i>o,p'</i>
1	$\text{H}_2\text{-mag}^b$	90		1.3		
2	$\text{PT}_{1.0}\text{-mag}$	90		1.8		
3	$\text{PS}_{1.0}\text{-mag}$	90	1.01	1.8	3.4 (3.4)	368
4	$\text{PS}_{1.0}\text{-mag}$	150	1.01	1.8	5.7 (5.7)	349
5	$\text{PS}_{0.6}\text{-PT}_{0.4}\text{-mag}^c$	90	0.66	1.8	5.0 (7.5)	141
6	$\text{PS}_{0.8}\text{-mag}$	90	0.78	1.6	1.7 (2.5)	203
7	$\text{PS}_{0.6}\text{-mag}$	90	0.66	1.5	1.0 (1.5)	128
8	$\text{AS}_{1.0}\text{-mag}$	90	0.97	2.2	10.1 (10.4)	458
9	$\text{AS}_{1.0}\text{-mag}$	150	0.97	2.2	47.7 (49.2)	260
10	$\text{PS}_{0.80}\text{-OD}_{0.20}\text{-mag}$	90	0.75	1.9	1.6 (2.4)	160

^aCalculated as mmol of *pp'* bisphenol A/mmol of SO_3H . ^bFully proton exchanged form of magadiite ($\text{H}_2\text{Si}_{14}\text{O}_{29}$). ^cIncompletely oxidized $\text{PT}_{1.0}\text{-mag}$.

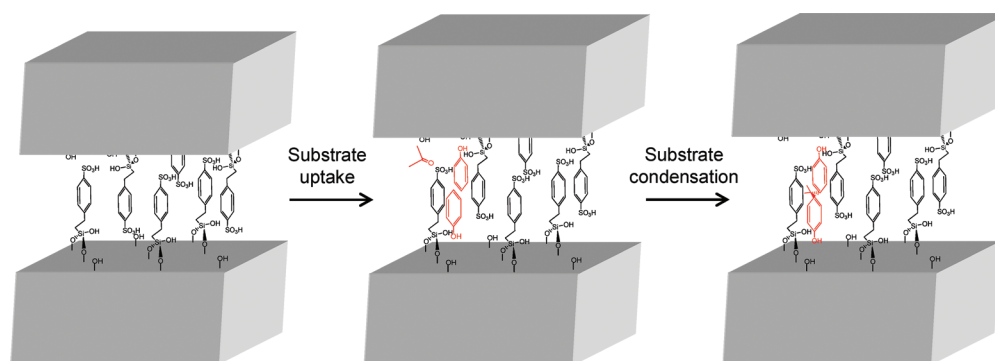


Figure 7. Schematic drawing of p,p' bisphenol A formation in the interlayer space of $AS_{1.0}$ -mag.

more effectively when the distance of the adjacent silyl group was smaller (Figure 7). Similar cooperative interactions between the surface of silylated layered materials and substrates have been reported in the selective adsorption of alkylalcohols on a layered silicate modified with the controlled amount of alkyl groups^{18–20} and that of 4-nonylphenol on layered silicate and titanate materials modified with alkyl and phenyl groups.^{21,24} The arylsulfonated magadiite showed higher p,p' bisphenol A yield than the propylsulfonated magadiites, possibly because the arylsulfonated material adsorbed a larger amount of phenol due to larger interlayer space and better affinity with phenol (due to π - π interactions). Judging from all results described, spatially arranged sulfonic acid plays an important role in positioning phenols so that the reactants condensed preferentially into p,p' bisphenol A (Figure 7).

In order to investigate the possible effect of the interlayer distance of PS_x -mag on the catalytic performance, magadiite modified with both propylsulfonic acid and octadecyl groups ($PS_{0.80}$ - $OD_{0.20}$ -mag) was synthesized, and then, the catalytic activity was compared to that of $PS_{0.8}$ -mag (Nos. 6 and 10, Table 1). It was found that the yield hardly varied with the interlayer space; on the other hand, the selectivity significantly decreased when the interlayer space was expanded with octadecyl group. This result supports again that the confined interlayer space of sulfonated magadiites plays an important role in the present phenomenon.

It was worth mentioning that the yield on propylsulfonated magadiite hardly changed when propylthiol was co-attached (Nos. 3 and 5, Table 2). This result suggests that few thiols cooperatively work to promote the present reaction and supports again that a geometrical effect by the interlayer confined nanospace plays an important role in the present phenomenon (Figure 7). Unlike the present case, in the thiol-assisted sulfonic acid-catalyzed reaction of phenol with acetone in mesoporous silica, the following mechanism has been proposed by some groups:^{34,37–39} carbonyl group of acetone is activated by a sulfonic acid and the adjacent thiol makes a nucleophilic attack, forming a strongly electrophilic carbon. This electrophilic carbon is regarded as a very bulky moiety because it is tethered on the pore wall; thus, the aromatic carbon at 4-position of phenol would approach the electrophilic carbon more easily than the carbon at 2-position. The second phenol would also approach a very bulky intermediate, forcing the aromatic carbon at 4-position to make a nucleophilic attack. This explains the high selectivity of p,p' bisphenol A over the o,p' isomer. The effect of spatially arranged arylsulfonic acid on the positioning phenols preferentially for the p,p' bisphenol A

formation is more predominant in $PS_{0.6}$ - $PT_{0.4}$ -mag (No. 5, Table 2).

CONCLUSIONS

We have reported the synthesis of silylated derivatives of a layered alkali silicate, magadiite, modified with propylsulfonic or arylsulfonic acid and the catalytic performance of the sulfonated magadiites for acid-catalyzed condensation of phenol with acetone into bisphenol A. The yield and selectivity of p,p' bisphenol A formation was successfully optimized by controlling the amount of the attached propylsulfonic or arylsulfonic acid, which correlated to the spatial distribution to make phenols arrange for the preferential condensation into p,p' bisphenol A. A wide variety of silane coupling reagents is attached on layered inorganic solids; therefore, the present results suggest the potential application of silylated layered materials for enzyme-like organic syntheses.

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Wiester, M. J.; Ulmann, P. A.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 2–26.
- (2) Ye, L.; Mosbach, K. *Chem. Mater.* **2008**, *20*, 859–868.
- (3) Wulff, G. *Chem. Rev.* **2002**, *102*, 1–27.
- (4) Margelefsky, E. L.; Seidan, R. K.; Davis, M. E. *Chem. Soc. Rev.* **2008**, *37*, 1118–1126.
- (5) Weiss, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 850–860.
- (6) Takagi, K.; Usami, H.; Fukaya, H.; Sawaki, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1174–1175.
- (7) Mortland, M. M. *J. Mol. Catal.* **1984**, *27*, 143–155.
- (8) Bergaya, F.; Lagaly, G.; Theng, B. K. G. Eds.; *Handbook of Clay Science*; Elsevier: London, 2006.
- (9) Pinnavaia, T. J. *Science* **1983**, *220*, 365–371.
- (10) Kim, T. W.; Hwang, S.-J.; Jhung, S. H.; Chang, J.-S.; Park, H.; Choi, W.; Choy, J.-H. *Adv. Mater.* **2008**, *20*, 539–542.
- (11) Ide, Y.; Matsuoka, M.; Ogawa, M. *J. Am. Chem. Soc.* **2010**, *132*, 16762–16764.
- (12) Alberti, G.; Casciola, M.; Constantino, U.; Vivani, R. *Adv. Mater.* **1996**, *8*, 291–303.
- (13) Kawasaki, T.; Omine, T.; Suzuki, K.; Sato, H.; Yamagishi, A.; Soai, K. *Org. Biomol. Chem.* **2009**, *7*, 1073–1075.
- (14) Ruiz-Hitzky, E.; Rojo, J. M. *Nature* **1980**, *287*, 28–30.
- (15) Osterloh, F. E. *J. Am. Chem. Soc.* **2002**, *124*, 6248–6249.
- (16) Ide, Y.; Ogawa, M. *Chem. Commun.* **2003**, 1262–1263.

- (17) Takahashi, N.; Kuroda, K. *J. Mater. Chem.* **2011**, *21*, 14336–14353.
- (18) Ogawa, M.; Okutomo, S.; Kuroda, K. *J. Am. Chem. Soc.* **1998**, *120*, 7361–7362.
- (19) Fujita, I.; Kuroda, K.; Ogawa, M. *Chem. Mater.* **2003**, *15*, 3134–3141.
- (20) Fujita, I.; Kuroda, K.; Ogawa, M. *Chem. Mater.* **2005**, *17*, 3717–3722.
- (21) Ide, Y.; Ogawa, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 8449–8451.
- (22) Ide, Y.; Ozaki, G.; Ogawa, M. *Langmuir* **2009**, *25*, 5276–5281.
- (23) Fuse, Y.; Ide, Y.; Ogawa, M. *Polym. Chem.* **2010**, *1*, 849–853.
- (24) Ide, Y.; Iwasaki, S.; Ogawa, M. *Langmuir* **2011**, *27*, 2522–2527.
- (25) Ide, Y.; Ogawa, M. *Chem. Lett.* **2005**, *34*, 360–361.
- (26) Ide, Y.; Ogawa, M. *J. Colloid Interface Sci.* **2005**, *296*, 141.
- (27) Takahashi, N.; Hata, H.; Kuroda, K. *Chem. Mater.* **2010**, *22*, 3340–3348.
- (28) Mochizuki, D.; Kowata, S.; Kuroda, K. *Chem. Mater.* **2006**, *18*, 5223–5229.
- (29) Eugster, H. P. *Science* **1967**, *157*, 1177–1180.
- (30) Brindley, G. W. *Am. Miner.* **1969**, *54*, 1583–1591.
- (31) Lagaly, G.; Beneke, A.; Wiess, A. *Am. Miner.* **1975**, *60*, 642–649.
- (32) Jerabek, K.; Hun, L. G.; Setinek, K. *Collect. Czech. Chem. Commun.* **1989**, *54*, 321–325.
- (33) Dufaud, V.; Davis, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 9403–9413.
- (34) Zeidan, R. K.; Dufaud, V.; Davis, M. E. *J. Catal.* **2006**, *239*, 299–306.
- (35) Margelefsky, E. L.; Zeidan, R. K.; Dufaud, V.; Davis, M. E. *J. Am. Chem. Soc.* **2007**, *129*, 13691–13697.
- (36) Margelefsky, E. L.; Bendjeriou, A.; Zeidan, R. K.; Dufaud, V.; Davis, M. E. *J. Am. Chem. Soc.* **2008**, *130*, 13442–13449.
- (37) Shimizu, K.; Kontani, S.; Yamada, S.; Takahashi, G.; Nishiyama, T.; Satsuma, A. *Appl. Catal. A* **2010**, *380*, 33–39.
- (38) Kubota, Y.; Jin, C.; Tatsumi, T. *Catal. Today* **2008**, *132*, 75–80.
- (39) Chen, C.-C.; Cheng, S.; Jang, L.-Y. *Microporous Mesoporous Mater.* **2008**, *109*, 258–270.
- (40) Ide, Y.; Ogawa, M. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1624–1629.
- (41) Kosuge, K.; Yamazaki, A.; Tsunashima, A.; Otsuka, R. *J. Ceram. Soc. Jpn.* **1992**, *100*, 326–331.
- (42) Aznar, A. J.; Sanz, J.; Ruiz-Hitzky, E. *Colloid Polym. Sci.* **1992**, *270*, 165–176.
- (43) Sohmiya, M.; Sugahara, Y.; Ogawa, M. *J. Phys. Chem. B* **2007**, *111*, 8836–8841.
- (44) Melero, J. A.; Van Grieken, R.; Morales, G. *Chem. Rev.* **2006**, *106*, 3790–3812.
- (45) Shylesh, S.; Wagner, A.; Seifert, A.; Ernst, S.; Thiel, W. R. *Chem.—Eur. J.* **2009**, *15*, 7052–7062.
- (46) Jerome, F.; Pouilloux, Y.; Barrault, J. *ChemSusChem* **2008**, *1*, 586–613.
- (47) Yanagisawa, T.; Kuroda, K.; Kato, C. *React. Solids* **1988**, *5*, 167–175.
- (48) Kudo, A.; Sakata, T. *J. Phys. Chem.* **1995**, *99*, 15963–15967.
- (49) Honma, T.; Toda, K.; Ye, Z.-G.; Sato, M. *J. Phys. Chem. Solids* **1998**, *59*, 1187–1193.
- (50) Mizukami, N.; Tsujimura, M.; Kuroda, K.; Ogawa, M. *Clays Clay Miner.* **2002**, *50*, 799–806.
- (51) Ogawa, M.; Ide, Y.; Mizushima, M. *Chem. Commun.* **2010**, *46*, 2241–2243.