# Switching catalytic reaction conducted in pore void of mesoporous material by redox gate control†

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**A molecular gate attached on the pore outlet of a mesoporous material, which is opened and closed by redox system of thiol groups, effectively switched the progress of a catalytic reaction promoted by the acidic site in the pore void.**

The ordered pore voids of mesoporous matrices provide designed systems at the molecular and nanometer levels. These pore structures exhibit specific and interesting transport of molecules in the pore voids.[1] Recent research on molecular transfer using these materials has focused on how to control the diffusion of molecules from pore voids to the exterior. The main applications of this technology are drug delivery and related systems.[2] After studies on the sustained release of molecules from mesopores,[3] some responsive-gate systems were reported.[4,5] The uniform pore sizes of mesoporous materials such as MCM-41 are advantageous for controlling the gating of pores, to achieve the effective control of molecular release. Our previous report of photo-responsive controlled release by coumarin-modified mesoporous silica is related to this technology.[5] In all of the cases mentioned above, the direction of molecular diffusion is from the pore interior to the exterior. It is also expected that the approach of molecules from the pore exterior to the interior is regulated by pore gating systems. One possible application of this reverse molecular transport is the control of catalytic reactions conducted in pore voids. This system may provide a new and general method for controlling heterogeneous catalytic reactions using porous materials. In this communication, we wish to briefly demonstrate a prototype for the switching of the progress of a catalytic reaction in the pores of a mesoporous material, where the redox reaction between disulfide and thiol dominates the outlet gating of the pores (Fig. 1).

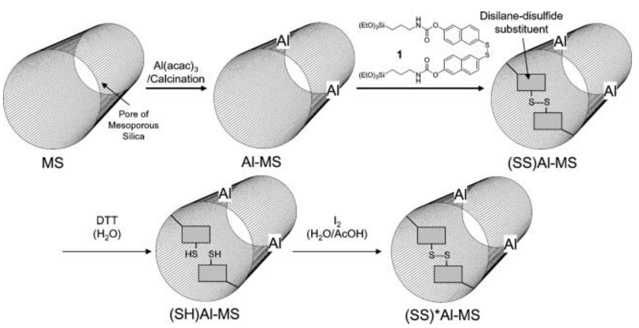

**Fig. 1** Scheme of mesoporous materials modified with a redox-responsive disulfide group.

The most common catalytic reaction using mesoporous silica materials is an acid-catalyzed reaction by Brønsted acidic sites created with the isomorphous loading of different atoms.[6] Recently, Si-MCM-41 was claimed to promote some acid-catalyzed reactions, which occur on the entire surface.[7] Since the aim of this study was to control a catalytic reaction by a pore gating system, only catalytic reactions that occur inside the pore are suitable. Therefore, we chose the dimerization reaction of α-methylstyrene (AMS) shown in Fig. 2.[8] While this reaction readily proceeds with a strong acid, no weak acids catalyzed this. As mentioned later, we verified that no reaction occurred with Si-MCM-41. Furthermore, simple dimerization with a single reactant is advantageous for monitoring the approach of molecules into the pore. An M41s-type of mesoporous silica (named MS) obtained by hydrothermal treatment with hexadecyltrimethylammonium bromide and subsequent calcination was transformed to Al-loaded (approximately 6 mol% of Al to Si) mesoporous silica using Al(acac)$_3$ (named Al-MS). Al-MCM-41-type materials are reported to be active in catalyzing AMS dimerization.[8] Although the direct synthesis (one-pot synthesis) from a mixed gel of Si and Al sources is common for the preparation of Al-MCM-41, this method often decreases the structural regularity of materials. Therefore, we employed a post synthesis method[9] using Al(acac)$_3$. Although the highly acidic catalytic site induced by Al atom is thought to be distributed evenly on the surface of mesoporous silica, the outer surface is negligible compared to the inner surface. This catalytic reaction is considered to occur exclusively in the pore, and is dominated by a pore gating system.

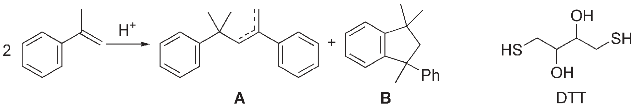

**Fig. 2** Dimerization of AMS and structure of DTT.

The steps for the transformation of mesoporous materials are summarized in Fig. 1 and experimental procedures are described in detail in the ESI.† A disilane–disulfide compound (**1**) readily produced by the direct reaction of 6-hydroxy-2-naphthyl disulfide with 3-(triethoxysilyl)propyl isocyanate was grafted (approximately 3 wt% according to TGA measurement) on Al-MS to form a disulfide-modified mesoporous material [(SS)Al-MS]. Our previous reports[5] revealed that the density of coumarin substituent on the surface of mesoporous silica is a crucial factor in a

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**Table 1** Profiles and catalytic activities of mesoporous materials[a]

| Catalyst | $d_{100}$/nm | SSA[b] /m$^2$ g$^{-1}$ | PPD[c] /nm | PV[d] /ml g$^{-1}$ | Yields (%) A | Yields (%) B |
|---|---|---|---|---|---|---|
| MS | 3.96 | 909 | 2.74 | 937 | 0.1 | <0.1 |
| Al-MS | 3.86 | 797 | 2.52 | 779 | <0.1 (8.6)[e] | >99.0 (85.5)[e] |
| (SS)Al-MS | 3.87 | 769 | 2.52 | 722 | 0.4 (0.9)[f] | <0.1 (<0.1)[f] |
| (SH)Al-MS | 3.84 | 742 | 2.52 | 739 | 1.7 (59.7)[e] | 97.1 (37.5)[e] |
| (SS)*Al-MS | 3.84 | 709 | 2.52 | 727 | 0.1 (1.5)[f] | <0.1 (0.2)[f] |

[a] AMS 1 mmol, catalyst 20 mg, toluene 5 mL, 120 °C, 2 h. [b] Specific surface area by the BET method. [c] Peak pore diameter by the BJH method. [d] Pore volume by the BJH method. [e] 80 °C, 2 h. [f] 120 °C, 6 h.

successful gating system. Dense grafting of coumarin substituent promotes its photo-dimerization to form crosslinking, resulting in pore closure. However, a sparse coumarin substituent is unfavorable for dimerization and does not induce closure of the pore. Our current conditions using a disilane–disulfide compound **1**, which forms crosslinking directly in the pore, is expected to be more effective for construction of a gating system. The results of AMS dimerization using various catalysts are summarized in Table 1. Mesoporous silica (MS; similar to Si-MCM-41) had no catalytic activity due to the absence of highly acidic sites. On the other hand, an AMS dimer (product **B**) formed by an intramolecular Friedel–Crafts reaction was obtained quantitatively by Al-MS at 120 °C for 2 h. When the disulfide-modified Al-MS [(SS)Al-MS] was used for this reaction, no dimers of AMS were obtained under the same reaction conditions, and most of the AMS was recovered. Even with a longer reaction time (6 h), no increase in product yields was detected. It is thought that the disulfide substituent prevented AMS from accessing the acidic site inside the pore, resulting in no formation of AMS dimers. The molecular length of compound **1** was estimated to be approximately 2.8 nm, which is too large to penetrate deeply into a pore of about 2.5 nm in diameter. Although the intimate arrangements of grafted substituents remain unknown, the disulfide substituent was likely to be attached mainly to the outer surface and in the vicinity of the pore outlet. These substituents effectively cover pore outlets to interfere with the access of AMS to catalytic sites.

Dithiothreitol (DTT) is often used for the cleavage of disulfide bonds to two thiol groups in protein and other chemistry.[10] (SS)Al-MS bearing a disulfide group was treated with DTT aqueous solution. Before this process, we had confirmed no activity of DTT for this dimerization. Using the obtained material [(SH)Al-MS], AMS dimerization proceeded in high yield at 120 °C (97.1%). However, the yield of Friedel–Crafts AMS dimer (**B**) at 80 °C (37.5%) was considerably lower than that of Al-MS (85.5%). Friedel–Crafts dimer **B** is produced sequentially *via* dimers **A**.[8] Next, this sample [(SH)Al-MS] was treated with an $I_2$ solution of $H_2O$/AcOH[11] to convert the thiol groups into a disulfide bond [(SS)*Al-MS]. As residual $I_2$ and HI promote the dimerization reaction, this sample was washed with water and ethanol thoroughly before use. AMS dimerization reaction using this (SS)*Al-MS resulted in the poor formation of dimers even in a longer reaction. Thus, AMS dimerization was effectively controlled by redox treatments.

A series of control experiments was also examined using Al-MS. Al-MS was treated with DTT in a similar manner to (SS)Al-MS. Then, this sample was mixed in the $I_2$ solution of $H_2O$/AcOH. These two catalysts thus treated without disilane substituent promoted the dimerization reaction as well as Al-MS. Therefore, the redox processing did not influence the catalytic activity of Al-MS for AMS dimerization. We also modified the sample MS (mesoporous silica without Al) using a disilane–disulfide compound **1**, and a series of treatments in a similar fashion to Al-MS was performed. In all catalytic reactions using these Al-free three samples corresponding to (SS)Al-MS, (SH)Al-MS and (SS)*Al-MS, no AMS dimers were formed. Therefore, no catalytic activities of disilane substituents themselves (in both disulfide and thiol forms) were confirmed as well.

There are no clear differences in the $d_{100}$ interplanar spacing of XRD patterns among the various samples in Table 1. Fig. 3A shows BJH pore-size distribution plots of some samples [Al-MS, (SS)Al-MS, (SH)Al-MS and (SS)*Al-MS]. The decrease of pore volume was observed from Al-MS to (SS)Al-MS. However, there

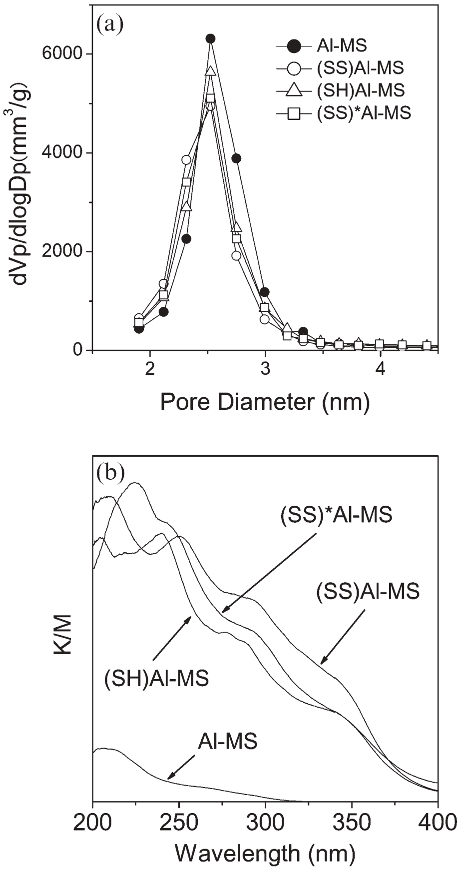

**Fig. 3** BJH pore-size distribution plots (A) and DR-UV spectra (B) of Al-MS, (SS)Al-MS, (SH)Al-MS, (SS)*Al-MS.

were no significant differences among three grafted catalysts [(SS)Al-MS, (SH)Al-MS and (SS)*Al-MS]. Similar observations are also found in mesoporous silica samples with a coumarin gate system.[5] The access of nitrogen into the pores is not influenced by the state of the gate substituent. Therefore, the situations of the whole pore voids did not change by redox treatments. Fig. 3B shows diffuse reflectance UV spectra of four samples. In modified samples, UV absorptions derived from disilane substituents were observed from 250 to 400 nm. The samples (SS)Al-MS and (SH)Al-MS had UV absorptions at about 250 nm and 235 nm, respectively. These absorptions are assigned to disulfide or thiol groups.[12] These are consistent with the expected bonding states of (SS)Al-MS and (SH)Al-MS. In (SS)*Al-MS, the absorption of the S–H bond disappeared and that of the S–S bond was regenerated at around 250 nm.

All results mentioned above support our concept shown in Fig. 1 that for the progress of a catalytic reaction in the pore, voids can be switched by the outlet gating of the pores. The high yields of the dimers observed in the reaction using (SH)Al-MS were caused by the change of the gate substituents. The cleavage of the disulfide substituent by DTT opened the outlet of the pore, which permitted the reactant to penetrate the catalytic site. The modest decrease of the catalytic activity of (SH)Al-MS might be induced by substituents in thiol form that still remain on the surface. Even after cleavage of the disulfide bond, thiol-substituents approximately 1.4 nm long interfered with the access of AMS to impair dimerization. On the other hand, in the case of (SS)*Al-MS, the thiol groups of (SH)Al-MS were oxidized by $I_2$ to disulfide. The poor yields of AMS dimers were due to re-closure of the pore gate. Thus, a gating system composed of disulfide–thiol redox switched the progress of AMS dimerization.

In this communication, we have shown that the catalytic activity of mesoporous materials can be reversibly controlled by the gating effect of a disulfide substituent on the pore surface.

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