Deodorization of *tert*-Butylmercaptan by Silica Aerogel Impregnated with Cu(II) and Mn(IV)

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Mercaptan compounds have very strong stench that gives unpleasant sensation to human olfactory nerves. As a few examples of such malodorant mercaptan compounds, methyl mercaptan and *tert*-butylmercaptan (TBM) can be considered to be related to our everyday life. Methyl mercaptan is a major gas product from overly fermented Kimchi product, which generates very unpleasant smell around our living space. For this reason, many companies which produce home appliances have participated in research activities to invent means to deodorize this compound.[1-3] TBM also has very unpleasant smell. For safety reason, TBM has been intentionally mixed as a gas odorant to liquified natural gas or liquified propane gas, together with tetrahydrothiophene, in order to give strong stench to the flammable gases.[4] Sometimes, leak of the gas odorant during the mixing process gives wrong alarm around the mixing facility. Presently, the leak is being removed by using activated carbons. In an attempt to devise different way to eliminate the leak, a catalytic adsorbent was synthesized by using silica aerogel as a support for the metal oxide overlayer which was active toward deodorization of TBM.

Figure 1 schematically describes the synthesis of silica aerogel and of the catalytic adsorbent. In an 100 mL three necked creased round-bottomed flask which was connected to argon, 0.1 M $Mg(OMe)_2$ solution was prepared by reacting 0.73 g Mg turnings with 300 mL dried methanol. By a gastight syringe, 67 g TEOS (99.9+%) was added to the solution. $Mg(OMe)_2$ was used as a catalyst for hydrolysis of TEOS.[5] Hydrolysis of TEOS was carried out by dropwise addition (during 10 h) of 8.0 g 30% H_2O_2 diluted in 100 mL dried methanol. Condensation of TEOS was completed by dropwise addition (during 10 h) of 2.7 g H_2O diluted in 100 mL dried methanol, getting a hazy silica sol. The silica sol, 200 mL, was loaded and sealed in an autoclave whose initial pressure was adjusted into 80 psi using nitrogen. Temperature and pressure of the sol was raised to 265 °C and 1200 psi, and solvent was removed at its critical state through the vent.[6] The white fluffy aerogel of silica was further dried in an oven at 120 °C overnight. The silica aerogel which was obtained by the way will be designated as AG-SiO_2. Active layer of Mn-Cu composition was applied on the surface of the AG-SiO_2 by impregnation. The AG-SiO_2 powder, 1.64 g, was well dispersed in a solution of metal salts prepared by dissolving 0.66 g $Mn(NO_3)_2 \cdot 4H_2O$ (8 w%) and 0.16 g $Cu(NO_3)_2 \cdot 3H_2O$ (2.5 w% to SiO_2) in 100 mL distilled water. Brown powder was obtained by removing water from the mixture by evaporation at elevated temperature. Calcination was carried out by heating the powder at 400 °C for 12 h in the flow of air, getting dark brown powder of the catalytic adsorbent, which will be designated as [Mn/Cu]AG-SiO_2.

The pore characteristics of the solid samples were investigated by carrying out porosimetry on the AG-SiO_2 and the [Mn/Cu]AG-SiO_2. Figure 2 shows the isotherms of nitrogen adsorption-desorption on the powder samples. The AG-SiO_2 exhibited isotherm curves in type II, before and after the heat treatment. The type II depicts for the solids with mesopores and macropores.[7] By seeing the first infliction was raised, these mesoporous solids also had some fraction of micropores. Comparing to a monolithic silica aerogel which had large fraction of micropores,[8] the powdery AG-SiO_2 synthesized in this study by using -MgOOH as catalyst had much less micropores. When the AG-SiO_2 was heated at 400 °C without being impregnated, the pattern of the hysteresis did not change. The type H1 hysteresis of the isotherms indi-

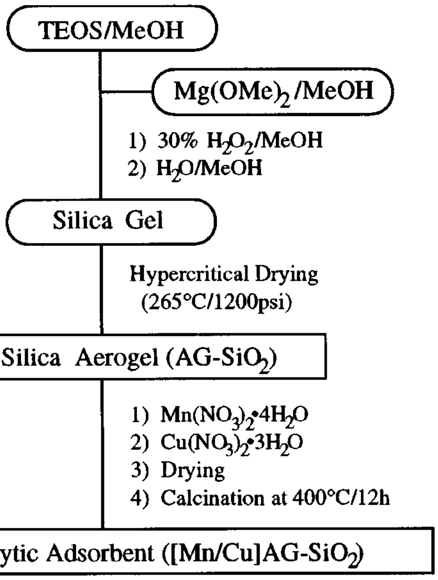


Figure 1. Schematic outline of the preparation of silica aerogel (AG-SiO_2) and the catalytic adsorbent ([Mn/Cu]AG-SiO_2). The AG-SiO_2 was prepared by using -MgOOH as hydrolysis catalyst.

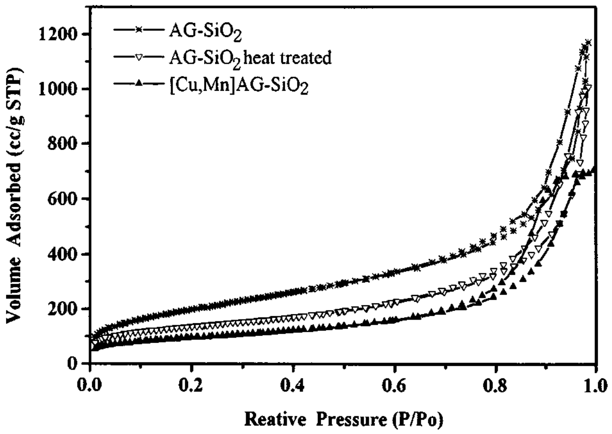


Figure 2. Isotherm curves of nitrogen adsorption and desorption on the surface of the solid samples. The curve marked by × is for AG-SiO_2, by △ for AG-SiO_2 heated at 400 °C, and by ▼ for [Mn/Cu]AG-SiO_2.

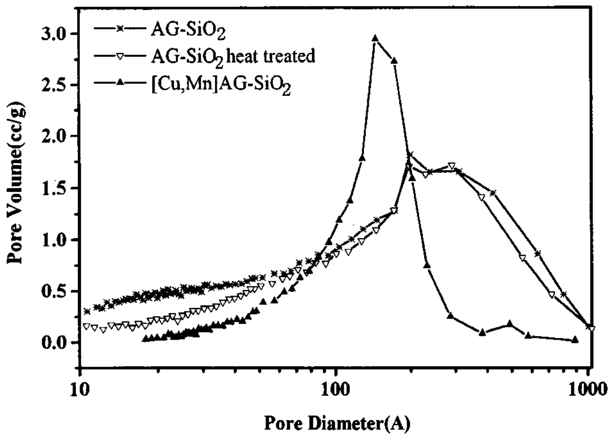


Figure 3. Size distribution of the pores in the solid samples. The curve marked by × is for AG-SiO_2, by △ for AG-SiO_2 heated at 400 °C, and by ▼ for [Mn/Cu]AG-SiO_2.

cated that the shape of the pore was cylindrical.[9] By seeing the isotherm was dragged down to lower value of the adsorbed volume over the whole pressure range, some of the pores were apparently eliminated. The values of the surface areas were provided in Table 1. Total surface area (S_t) was calculated by BET method,[7] and the micropore surface area (S_{micro}) was calculated by using the slope of t-plots derived from the isotherms.[7] The calculated values of the surface area indicated that significant loss of total surface area was brought on by demise of both the micropores and mesopores.

Pore size distribution was analyzed from desorption isotherm by BJH method,[9] and provided in Figure 3. Desorption isotherm was also used for the [Mn/Cu]AG-SiO_2 to get the neck-dimension of the nearly ink-bottled pores (see below). It was shown that the closure of the pores occurred significantly below 30 Å, and it did not occur above 50 Å. Assessing from the dimension, it was presumed that the closure of the pores occurred mainly through interlayer condensation reaction among ≡Si-OH moieties along the adjacent walls. The variation of BET surface area during heat-treatment was shown in Table 2. The major loss of the surface area occurred below 200 °C. Thermogravimetric analysis also showed that the major weight decrease was observed below 200 °C. These observations corroborated the closure of the pores by the interlayer condensation, which was accompanied by the elimination of chemisorbed water below 200 °C.

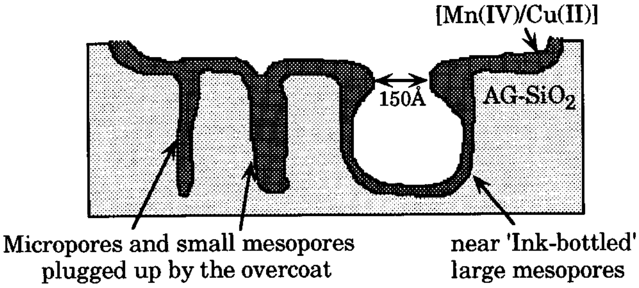
Table 1. Surface areas calculated from the isotherm of nitrogen adsorption-desorption, and from t-plots derived from the isotherms

Sample	S_t (m^2/g)	S_{micro}	S_{meso}
AG-SiO_2	741	118	623
AG-SiO_2 heated	490	46	444
[Mn/Cu]AG-SiO_2	344	24	320

Table 2. Variation of the surface area of the solid samples upon being heated in the flow of air

Temperature	AG-SiO_2	[Mn/Cu]AG-SiO_2
as prepared	734 m^2/g	-
200 °C	491	325
300 °C	400	311
400 °C	431	300
500 °C	442	300

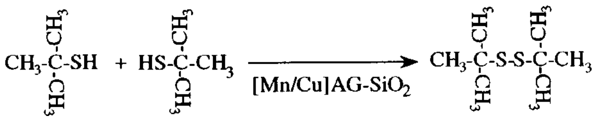
When heat-treatment was carried out after impregnation of transition metal constituents, surface area decreased further down to 344 m^2/g. The hysteresis of the isotherm changed its shape from H1 to near type H2, which represented 'ink-bottled' pores.[9] Apparently, the thickness of the impregnated layer was thicker over the neck of the pores, thereby, transforming cylindrical pores into near 'ink-bottled' ones. Surface area (Table 1) calculated from t-plots indicated that most of the micropores were eliminated. Pore size distribution in the Figure 3 also showed that the pores below 40 Å were nearly absent, which indicated that most of the micropores and small mesopores were eliminated. At the same time, the size of the large mesopores, which was calculated from the desorption isotherm curve, shifted from 250 Å down to 150 Å, and its distribution became narrower. These observations provided a glimpse at the pattern of the overcoat of the transition metal oxides over the silica aerogel. The overcoat plugged up most of those micropores and small mesopores, and narrowed the large mesopores into the ink-bottled shape, as suggested in the Scheme 1. It was not known whether the overcoat was a collection of particulates or a uniform layer in microscopic dimension. A form of layer was assumed in the Scheme, because population of macropore (*viz.* surface roughness which should have resulted from particulate formation) decreased after the active layer was applied. At least in macroscopic range, energy-dispersive spectroscopic measurements obtained from various points indicated the composition was fairly uniform. Surface images of the solid samples, observed by SEM, showed that the rugged surface of the AG-SiO_2 got smoother after it was impregnated, which corroborated the Scheme.



Scheme 1

Deodorization of TBM on the surface of the [Mn/Cu]AG-SiO_2 was measured by gas chromatograph equipped with a flame photometric detector. Into a 190 mL air-filled Schlenk vessel equipped with a Mininert syringe valve,[10] the powder sample was loaded on the bottom, and a pulse of TBM was injected over the sample into 500 ppm by using a gastight syringe, at room temperature. Immediately after the injection, a small fraction of the gas, 0.04 mL, was taken by a gastight syringe and injected to GC. Figure 4 showed the variation of the integrated peak area of TBM as time passed. Each peak corresponds to one pulse of 500 ppm TBM. It was observed that demise of the TBM peak occurred within less than 15 min over the [Mn/Cu]AG-SiO_2 at room temperature. The drop of the peak intensity was complete over the time, and no smell of TBM could be detected by sensual test at all. Therefore, TBM was converted to other compound which had no or less stench. It was observed that the [Mn/Cu]AG-SiO_2 also kept its reactivity during consecutive injections of TBM pulses.

After the injection of excess TBM, some smell was detected by sensual test. But, it was not of TBM, nor was unpleasant. FTIR measurement on this gas product showed that it was di-*tert*-butyldisulfide. GC-MS analysis on the gas product also corroborated the major gas product as di-*tert*-butyldisulfide. These observations suggested that deodorization of TBM proceeded mainly through dimerization of TBM into di-*tert*-butyldisulfide on the surface of the [Mn/Cu]AG-SiO_2, which was expressed in reaction (1).



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}SH + HS\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_3 \xrightarrow[\text{[Mn/Cu]AG-SiO}_2]{} CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}S\text{-}S\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_3 \quad (1)$$

In order to verify whether the transition metal constituents were playing an active role in the reaction, GC measurement was carried out over the AG-SiO_2 heated at 400 °C without being impregnated, whose the result was shown in Figure 5. The first pulse was not eliminated completely, showing persistent peak on GC measurement. Second pulse left more residual TBM which was remained over the AG-SiO_2. The amount of the residual TBM was not decreased over the hours, and sensual test over the vessel verified very strong stench by the residual TBM. Therefore, removal of TBM over the AG-SiO_2 was occurring simply by physisorption, not by chemisorption. On the other hand, the transition metal constituents in the [Mn/Cu]AG-SiO_2 were surely participating in the catalytic dimerization of TBM, thereby, the removal of TBM over the [Mn/Cu]AG-SiO_2 was occurring by chemisorption, at room temperature. X-ray photoelectron spectroscopic measurements on the surface of the [Mn/Cu]AG-SiO_2 showed that the oxidation states of the transition metals were Cu(II) and Mn(IV). Thermogravimetric analysis on the [Mn/Cu]AG-SiO_2 before and after the reaction with TBM showed a difference of the weight loss of around 7% below 150 °C, which suggested some of the di-*tert*-butyldisulfide generated by dimerization was remaining on the surface presumably as physisorbed.

As comparison, the GC experiment was also performed with the activated carbon which is presently being used in removing the leak. It took about an hour to remove most of the TBM injected over the activated carbon, and the removal was not complete by considering the TBM peak was persistently observed. The peak area after an hour increased as

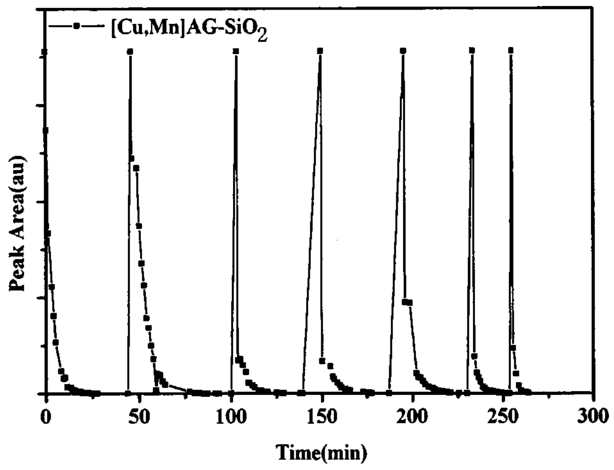


Figure 4. Decrease of the amount of TBM over [Mn/Cu]AG-SiO_2 measured by gas chromatograph. The graph shows the measurements on seven consecutive pulses of each 190 mL of 500 ppm TBM.

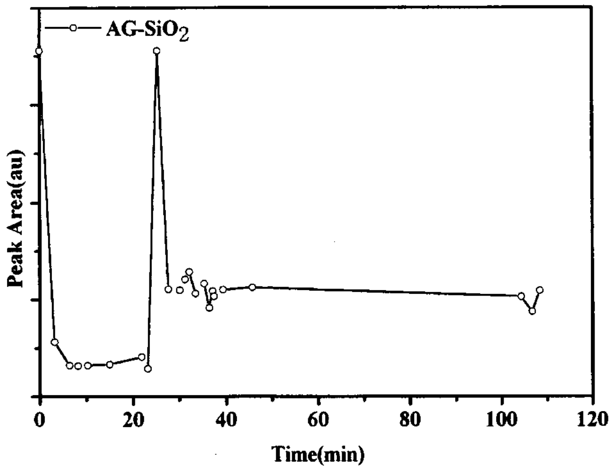


Figure 5. Variation of the amount of TBM over AG-SiO_2 measured by gas chromatograph. After the sudden initial drop, the remaining TBM persisted, and the amount of the residual TBM increased as additional pulse was injected.

several pulses were injected consecutively. Most of all, the residual TBM registered very strong sensation on sensual test, which indicated only physisorption was occurring over the activated carbon.

Study by others reported on bond breakage of dimethyldisulfide by reaction over the surface of metal oxide.[11,12] The dissociation of dimethyldisulfide proceeded at 300 °C, which indicated the reaction was endothermic. Therefore, the reaction (1) which is reverse reaction of the dissociation of di-*tert*-butyldisulfide is supposedly exothermic reaction. It raised possibility that the reaction (1) would proceed at room temperature if activation energy was provided, which turned out to be so.

In summary, TBM could be deodorized by using the catalytic adsorbent which was prepared by putting an active layer of Cu(II) and Mn(IV) over the silica aerogel synthesized via hypercritical drying of the silica alcogel. The pores of the aerogel below 40 Å diameter were eliminated by being plugged up by the active layer. Cylindrical mesopores became nearly 'ink-bottled' ones by the overlayer, and their size distribution became narrower. Major reaction occurring on the surface of the catalytic adsorbent was dimerization of TBM into di-*tert*-butyldisulfide which had no stench. The dimerization reaction didn't occur on the surface of either silica aerogel or activated carbon. Only physisorption of TBM was occurring on the surface of those two materials. The elimination of TBM over the catalytic adsorbent was complete and fast, that 190 mL of 500 ppm TBM was deodorized within 15 min and did not leave any stench. Further investigation on the mechanism of the dimerization, and on the means to utilize the catalytic adsorbent as an applicable way is on our pursue.

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