Dimerization of *tert*-Butylmercaptan over the Surface of Aerosil® Impregnated with Copper and Manganese

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A ceramic powder of destructive adsorbent was synthesized by impregnating copper and manganese on the surface of silica aerosil®. *In-situ* FTIR measurements on pulses of malodorant *tert*-butylmercaptan injected over the powder showed that *tert*-butylmercaptan dimerized into di-*tert*-butyldisulfide on the surface of the adsorbent in an ambient condition. GC/MS measurement on the gas over the adsorbent showed no *tert*-butylmercaptan remaining, and showed only the dimerization product of di-*tert*-butyldisulfide. Most of the dimerization product, di-*tert*-butyldisulfide, remained on the surface of the adsorbent as physisorbed condense, and apparently lowered the destruction efficiency by blocking the surface from the access by tert-butylmercaptan. Upon being heated above 100 °C, it was observed that the physisorbed di-*tert*-butyldisulfide dissociated back into *tert*-butylmercaptan. *Tert*-butylmercaptan physisorbed on the activated carbon, thereby no dimerization was occurring on the surface of the activated carbon. In an argon environment, the dimerization reaction was practically not occurring even on the surface of the adsorbent, indicating the free oxygen in air was also participating in the dimerization reaction. Water was identified as a by-product of the dimerization reaction. Possible reactions on the surface of the adsorbent were proposed.

Introduction

As the standard of living is improved, there has been much demand for making living conditions more comfortable than before. In order to meet such demand for comfortable living environment, 'malodor' has to be put under control.

Bad smell can be originated from various different sources. In many occasions, common sources of the bad smell around living space are foods. Especially, when the foods are rotten or over-fermented, the smell from them is very unpleasant. Especially in a few far-eastern countries, such as Korea and Japan, combined use of fish[1] and garlic[2] generates various malodorant volatile compounds. Most of those malodorant compounds fall into two categories, mercaptan derivatives and amine derivatives.

Commercially, there are many different ways to reduce the malodorant volatiles. Simply, those compounds can be removed by adsorbents with high surface area, such as activated carbons or zeolites. Many commercial deodorizing products in the market use one of these materials. Because the malodorants are removed only by physisorption, the lifetime of the adsorbents are very limited. Malodorants can also be removed by reaction with oxidizing agent, such as ozone.[3] The electronic device, which is used for generating ozone, consumes electric energy.

The malodorants can be removed without energy consumption, if *via* the catalytic reaction. As a possible way to get rid of malodorant alkyl-mercaptan compounds, we reported catalytic reaction of *tert*-butylmercaptan (TBM) on the surface of silica aerogel impregnated with Cu(II) and Mn(IV) in our previous communication.[4] TBM is currently being used as gas-odorant to give strong stench (rotten onion) to liquefied natural gas (LNG), which is originally odorless, as a safety alarm against leak.[5] Here, we report further details into the reaction mechanism of dimerization of TBM occurring on the surface of the catalytic adsorbent.

Experimental Section

Commercially obtained silica aerosil® was used as the support for the catalytic adsorbent. A few grams of the silica aerosil® powder was soaked in an aqueous solution of $Cu(NO_3)_2$ and $Mn(NO_3)_2$. Weight of copper and manganese was 4% and 8% to silica, respectively. By removing excess water by evaporation around 70-80 °C, thick wet paste was obtained. The paste was dispersed on aluminum foil, and further dried into thin crusts in an oven at 120 °C. Brief grinding in an agate mortar turned the crusts into fine brown powder. The catalytic adsorbent was prepared by calcining the brown powder at 400 °C for 10hs in ambient air, and was designated as [Cu/Mn]AS-SiO_2. When needed, gas environment was controlled by using a tube furnace, during calcination. Several different kinds of gases, such as nitrogen, oxygen, or 4% H_2/Ar, were used. Good ventilation is recommended during calcination, because toxic nitrogen oxides are produced by decomposition of nitrates.

Dimerization reaction of *tert*-butylmercaptan (TBM) was monitored by in-situ obtaining FTIR spectra from head-gas over [Cu/Mn]AS-SiO_2, using Nicolet Impact 400. In a cylindrical gas cell (2.5 cm dia. × 10 cm long) which had two stopcocks attached, 100 mg of [Cu/Mn]AS-SiO_2 powder was placed on the bottom, and covered with homemade glass cover to prevent the fluffy powder from electrostatically flying around. Into the cell, a pulse of TBM was injected through the stopcock by using a gas-tight syringe. Initial concentra-

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tion of TBM was adjusted to 500 ppm. Immediately after the injection, FTIR spectra were taken every 5 min. After TBM was consumed, additional pulses were injected, and the measurement was repeated for the pulses. In order to attest the involvement of environmental gas to the reaction, the cell was filled with argon, or with oxygen, prior to the TBM injection.

Gas product was characterized by gas-chromatograph/mass-spectrometry (GC/MS), using Finnigan Automass 300. In a homemade flask reactor, liquid TBM was in-situ evaporated over [Cu/Mn]AS-SiO_2, thereby, obtaining sufficient amount of gas product for GC/MS analysis. Gas chromatograph (GC) was carried out with Varian 3400, which was equipped with a flow-bed reactor 5 cm dia. × 10 cm long) and the flame photometric detector. Powder sample of the [Cu/Mn]-AS-SiO_2 was made into pellets, and loaded in the flow bed reactor. Gaseous TBM was introduced into the reactor by passing diluent gas, He, through liquid TBM in a flow rate of 300 mL/min.

Surface morphology of [Cu/Mn]AS-SiO_2 was deduced from adsorption and desorption behavior of nitrogen measured by Micromeritics ASAP 2400. BET surface area was calculated by BET method.[6] Pore size distribution was calculated from isotherm curve of nitrogen desorption by BJH method.[7]

Results and Discussion

In previous communication,[4] dimerization reaction of *tert*-butyl mercaptan (TBM) was carried out on the surface of silica aerogel impregnated with Cu(II) and Mn(IV). In this report, commercially obtained silica aerosil® was used as a cost-effective support instead of the aerogel, in economical reason. Whereas surface area of the aerogel was 740 m^2/g, that of aerosil® was only 200 m^2/g. When they were calcined at 400 °C, surface area of those samples decreased down to 300 m^2/g and 190 m^2/g for calcined aerogel and aerosil®, respectively. Therefore, aerosil® could replace aerogel without much difference in surface area.

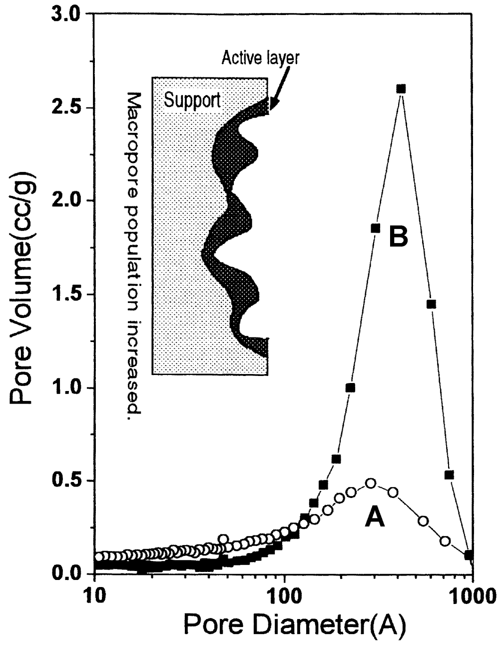

Figure 1. Pore size distribution of the aerosil® (A) and [Cu/Mn]-AS-SiO_2 (B), calculated from desorption isotherm by BJH method. The suggested surface morphology was shown in the inlet.

Figure 1 compares pore size distribution of the aerosil® with that of [Cu/Mn]AS-SiO_2. It was observed that mesopores below 100 Å were eliminated after the impregnation, which indicated that the overcoat of copper and manganese oxides plugged all those mesopores up. With the demise of the mesopores, volume of macropores above 100 Å was largely increased. Average size of the macropores was not changed by the impregnation, though. This observation indicated that the depth of those macropores got deepened as aerosil® was impregnated with copper and manganese. Thereby, the adsorbed volume was increased. This morphological alteration of the surface is schematically shown in the inlet of the figure.

Diminishing TBM over the [Cu/Mn]AS-SiO_2 was *in-situ* monitored by observing FTIR spectrum of the overhead gas. Figure 2 shows variation of the FTIR spectrum over time

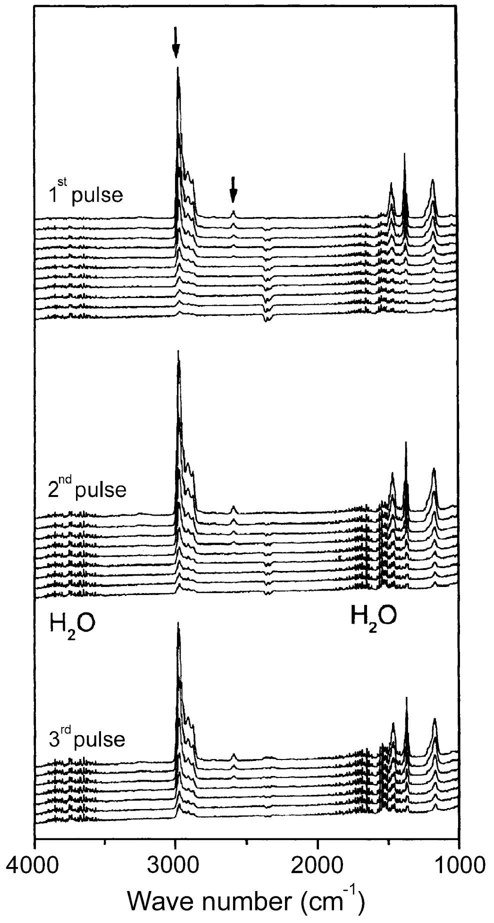

Figure 2. FTIR spectra taken from three consecutive pulses (500 ppm/each pulse) of TBM over the [Cu/Mn]AS-SiO_2. The measurement was carried out continuously, so that the lapse between consecutive spectra was 2 min. Each cluster of the spectra represents disappearance of one pulse of TBM. The peaks marked by arrows provide guide to discern TBM from DBDS.

measured for three consecutive pulses of TBM injected over the [Cu/Mn]AS-SiO_2. Each spectral cluster shows complete elimination of one pulse (500 ppm) of TBM over 100 mg powder of the [Cu/Mn]AS-SiO_2. Span of time for each cluster was about 20 min. The spectrum with feeble intensity after 20 min (the last spectrum of each cluster) was for dimerization product, di-*tert*-butyl disulfide (DBDS). Because FTIR spectrum of TBM is very similar to that of DBDS, a careful comparison is needed to discern reactant from product. The best guidance is provided by the peaks at 2600 cm^{-1} and 2990 cm^{-1} in the spectrum of TBM. The spectrum of DBDS is devoid of the peaks. As was observed with [Cu/Mn]AG-SiO_2,[4] removal of malodorant TBM on the surface of the [Cu/Mn]AS-SiO_2 was complete in about 20 min. After the time, a sensual test over the open vessel registered no stench from malodorant TBM at all.

Apparently, only a small fraction of DBDS was detected by FTIR, by seeing the feeble intensity of the spectrum. Considering vapor pressure of DBDS (2.45 kPa at 25 °C) was much lower than that of TBM (24.2 kPa at 25 °C), it was suggested that DBDS would preferentially condense into the pore. In order to get a definitive identification of the product, gaseous overhead was analyzed by GC/MS. Gas chromatograph of the gaseous overhead is shown in Figure 3A. Only a major product was DBDS, and no TBM was remained.

As comparison study, in-situ monitoring was also carried out for pulses of TBM injected over the activated carbon. It took more than 40 min until FTIR spectrum registered not much of TBM. The removal of TBM over the activated carbon was incomplete even after an hour. As more pulses were injected, the amount of the remaining TBM increased. Sensual test over open vessel registered very strong stench of remaining TBM over the activated carbon, whereas no such smell could be sensually detected over the [Cu/Mn]AS-SiO_2. Gas chromatograph of the overhead gas in Figure 3B, obtained by GC/MS, showed that only TBM was detected, but not DBDS. Therefore, chemisorption of TBM was occurring over the surface of the [Cu/Mn]AS-SiO_2, whereas only physisorption was occurring over the activated carbon.

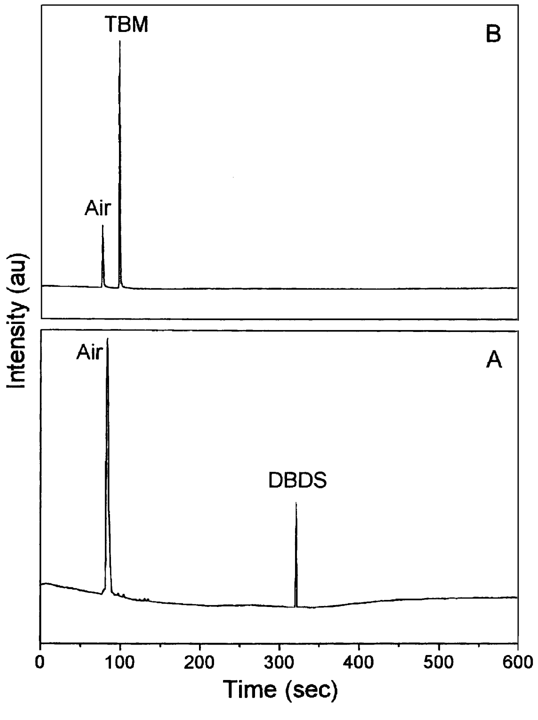

Figure 3. Gas chromatograph of the overhead gas obtained after TBM was injected over the [Cu/Mn]AS-SiO_2 (A), or over the activated carbon (B).

Dimerization of TBM into DBDS should have left hydrogen behind. But, molecular hydrogen was apparently not detected by GC. Figure 2 showed that water-peaks around 3700 cm^{-1} and 1700 cm^{-1} were gradually growing as TBM was dimerized into DBDS. Therefore, water was a byproduct of dimerization reaction of TBM on the surface of the [Cu/Mn]AS-SiO_2, which consumed hydrogen that was given off from TBM. As the reaction over the [Cu/Mn]AS-SiO_2 proceeded further, the amount of water in the overhead was slowly diminishing together with that of the DBDS (see figure 5 for DBDS). It is suggested that those two were removed by being adsorbed on the surface of the [Cu/Mn]AS-SiO_2 (see below).

In order to seek the oxygen source, the dimerization reaction was carried out in strictly controlled gas environment. Figure 4 shows the variation of in-situ obtained FTIR spectra in pure argon environment. When oxygen in the gas environment was eliminated, dimerization reaction of TBM was practically not occurring. Even after 2 days, the TBM peaks at 2600 cm^{-1} and 2990 cm^{-1} were still detected. When the reaction was carried out in pure oxygen, no TBM was left after 1h, as seen in the inlet. This observation provides strong evidence that molecular oxygen from environmental gas is reactant.

But, even in argon environment, where free oxygen was eliminated, the intensity of the TBM-peak was decreasing, even though it was over very long period. After a few days in argon environment, TBM was surely dimerized, by con-

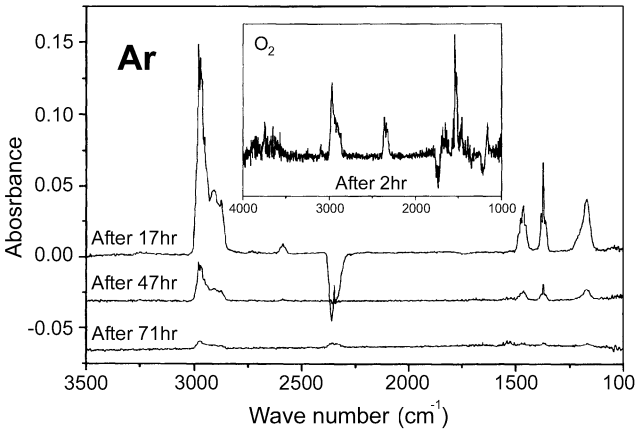

Figure 4. FTIR spectra taken from a pulse of TBM (500 ppm) injected over the [Cu/Mn]AS-SiO_2. The environment in the gas cell was pure argon. The arrows indicate unique peaks for TBM. The spectrum in the inlet shows those TBM peaks are not observable in oxygen environment.

Table 1. Elemental content in the [Cu/Mn]AS-SiO$_2$, before and after the injection of TBM over it. DBDS was generated by the dimerization of TBM over the surface, and it condensed in the pores. Upon being heated, the [Cu/Mn]AS-SiO$_2$ lost all the sulfur

Condition	sulfur (w%)	carbon	hydrogen
before the reaction	0	$<10^{-2}$	0.18
after the reaction (20 °C)	2.66	4.32	0.91
after the reaction (100 °C)	0	0.69	0.23

sidering sensual test registered no stench from TBM. This observation indicated that lattice oxygen on the surface of the [Cu/Mn]AS-SiO$_2$ could be another source for oxygen. Because dissociation energy of molecular oxygen is very high, it is not probable that molecular oxygen directly reacted with reactant. The surface of metal oxide should have provided catalytic sites for dissociation of the free oxygen. Scrambling of the oxygen from environment and that in the lattice was reported to be very fast.[8] ESR and Raman study on oxidative coupling of methane on Mn/W-impregnated silica reported lattice oxygen was responsible for the activation of methane.[9] IR study on catalytic oxidation of organics over metal oxide also suggested strong evidences on involvement of lattice oxygen in the reaction.[10] Likewise, lattice oxygen should have played an important role in the dimerization reaction of TBM on the surface of the [Cu/Mn]AS-SiO$_2$. It was also observed that surface reactivity toward dimerization of TBM was largely diminished when the [Cu/Mn]AS-SiO$_2$ was exposed to humidity for extended time. The surface reactivity was also largely diminished, when [Cu/Mn]-AS-SiO$_2$ was annealed in oxygen. These observations strongly indicated the involvement of surface defects to the dimerization reaction of TBM, together with the lattice oxygen.

Elemental data in Table 1 provided a glimpse to see whether sulfide would be fixated into the surface layer of the [Cu/Mn]AS-SiO$_2$ or not. After chemisorption of TBM on its surface, the [Cu/Mn]AS-SiO$_2$ contained fair amount of sulfur, together with hydrogen and carbon. Simple calculation readily showed the empirical formula to be C_4H_9S, which is for DBDS ($C_8H_{18}S_2$). Upon heating the sulfur containing sample above 100 °C, all the sulfur was eliminated. Therefore, most of the DBDS (together with water), which was produced by dimerization reaction of TBM, was remaining on the surface of the [Cu/Mn]AS-SiO$_2$ as physisorbed condense on its macropores. After the removal of DBDS from the surface by heating, some carbon and hydrogen were left behind, even though the amount of those was relatively small. This observation suggested that some DBDS was decomposed on the surface of the [Cu/Mn]AS-SiO$_2$, when it was heated.

To see if DBDS on the surface was decomposing upon being heated, thermal product was *in-situ* characterized by GC. Figure 5 shows the variation of integrated intensity of the GC peaks of TBM and DBDS during continuous influx of TBM over pelletized [Cu/Mn]AS-SiO$_2$ in a flow bed. Before the breakthrough reached (after around 200 min), all TBM was consumed by [Cu/Mn]AS-SiO$_2$. Fair amount of dimerization product, DBDS, was detected initially, but it decreased down to none after the breakthrough. This observation conforms to the previous suggestion that gaseous products were condensing on the surface of [Cu/Mn]AS-SiO$_2$. As the reactive surface of [Cu/Mn]AS-SiO$_2$ was blocked from TBM by physisorbed DBDS, the breakthrough reached, and TBM peak started appearing. After the influx of TBM was cut off, the [Cu/Mn]AS-SiO$_2$ in the reactor was heated at 200-300 °C, in order to see if adsorbed DBDS would be dissociated upon being heated. Immediately after the reactor was heated, sudden increase of TBM peak was observed, and no peak was observed for DBDS. Therefore, it was shown that DBDS dissociated back into TBM on hot surface of the [Cu/Mn]AS-SiO$_2$. This observation also confirmed that dimerization product was condensing in the macropores of the [Cu/Mn]AS-SiO$_2$, not being released into the overhead. It is suggested that the condensed DBDS blocked the active sites against TBM, thereby lowering the efficiency of the dimerization reaction of TBM on the surface of the [Cu/Mn]AS-SiO$_2$.

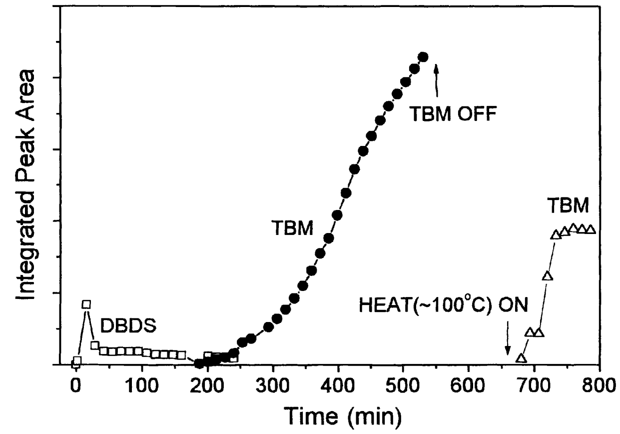

Figure 5. The integrated area of gas chromatograph peaks of TBM (●) and DBDS (□) in the effluent gas passing over the pelletized [Cu/Mn]AS-SiO$_2$ in the reactor. TBM (△) was *in-situ* generated from adsorbed DBDS when the [Cu/Mn]AS-SiO$_2$.was heated after the outside supply of TBM was cut off.

Study by others on the reaction of dimethyldisulfide on hot surface of metal oxide reported that it dissociated into methyl mercaptan.[11] On the surface of aluminum oxide, the dissociation of dimethyldisulfide reportedly occurred at 300 °C, indicating the reaction was endothermic. No report by others on dissociation of DBDS on metal oxides could be traced. Considering the reported precedent on dimethyldisulfide, it was suggested that DBDS was also endothermically dissociating on hot surface of the [Cu/Mn]AS-SiO$_2$. If not heated, DBDS would just slowly be desorbed as it was, without being dissociated. Because the dimerization reaction of TBM into DBDS is reverse reaction of the dissociation of DBDS into TBM, it was suggested that the dimerization of TBM proceeded exothermically. Therefore, it is anticipated that the dimerization reaction is going to readily occur at below freezing temperature (Cu and Mn impregnated aluminosilicate is currently being used as a commercial deodorant in a refrigerator).

Alkyl migration from phosphorous reactant to lattice oxygen was known to occur on the surface of magnesium oxide.[12] The study on the dissociation of dimethyldisulfide also reported that hydrogen needed for the dissociation reaction could be provided by decomposition of alkyl ligands (α-methylene), which generated many by-products.[13] Therefore, it was suggested that alkyl migration also occurred from DBDS to lattice oxygen of the [Cu/Mn]AS-SiO_2. Carbon and hydrogen remnants in the [Cu/Mn]AS-SiO_2 after heat-removal of DBDS (in Table 1) indicated that decomposition of the alkyl fragment provided hydrogen needed for the dissociation reaction of DBDS.

From the experimental observations described so far, the reaction mechanism of the dimerization of TBM, and of the dissociation of DBDS, on the surface of [Cu/Mn]AS-SiO_2 was proposed below. Stoichiometric reaction (1) and (2) summarized overall reactions occurring over the surface of the [Cu/Mn]AS-SiO_2.

$$2(CH_3)_3CSH + 1/2O_2 \xrightarrow[\sim \text{room temp.}]{} (CH_3)_3CSSC(CH_3)_3 + H_2O + \Delta H \tag{1}$$

$$(CH_3)_3CSSC(CH_3)_3 + 2H \xrightarrow[> 100\ ^\circ\text{C}]{} 2(CH_3)_3CSH - \Delta H \tag{2}$$

Conclusion

By impregnating copper and manganese on the surface of silica support, a catalytic adsorbent, [Cu/Mn]AS-SiO_2, was prepared. As for the support of the catalytic adsorbent, commercially obtained silica aerosil® was proved to be an appropriate substitute for the silica aerogel,[4] which was costly to synthesize.

Malodorant *tert*-butylmercaptan was chemisorbed on the surface of the [Cu/Mn]AS-SiO_2, and was dimerized into di-*tert*-butyldisulfide, which had no stench. On the contrary, it was merely physisorbed on the surface of activated carbon. It was shown that free oxygen was participating in the dimerization reaction of *tert*-butylmercaptan as a reactant. With the oxygen, the hydrogen abstracted from *tert*-butylmercaptan produced water. Many circumstantial evidences directed that lattice oxygen and surface defects also acted as active species in the reaction.

Most of the di-*tert*-butyldisulfide, which was produced by dimerization reaction of *tert*-butylmercaptan, remained physisorbed on the surface of the [Cu/Mn]AS-SiO_2. Upon being heated above 100 °C, di-*tert*-butyldisulfide dissociated back into *tert*-butylmercaptan on the surface of the [Cu/Mn]AS-SiO_2. Apparently, decomposition of alkyl moiety of di-*tert*-butyldisulfide provided hydrogen needed for the dissociation.

It was shown that malodorant *tert*-butylmercaptan could be removed at ambient condition without using any energy-consuming device, by catalytically dimerizing it into non-odorant disulfide. Therefore, the [Cu/Mn]AS-SiO_2 can be a good candidate for a deodorizing agent to remove malodorant alkylmercaptans, catalytically. But, a way to suppress the strong adsorption of in-situ produced disulfides on the surface of the adsorbents would have to be devised to raise the deodorizing efficiency of the agent.

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