

REMOVAL OF METHANETHIOL BY SEPIOLITE AND VARIOUS SEPIOLITE-METAL COMPOUND COMPLEXES IN AMBIENT AIR

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ABSTRACT

In ambient air having 60% relative humidity (RH) at 25°C, the adsorption of methanethiol by sepiolite was studied by comparison with that by coconut-shell active carbon. The amount of methanethiol adsorbed by sepiolite was as small as 0.12 $\mu\text{mol/g}$ in the air with 1 ppm methanethiol, while, the amount by active carbon was as large as $>1.1 \mu\text{mol/g}$ in the air with ≤ 0.03 ppm methanethiol. Methanethiol was converted into dimethyldisulfide on active carbon.

In ambient air having 60% RH at 25°C, the removal of methanethiol by the sepiolite-metal complexes was also studied by comparison with that by the corresponding metal compounds. The removal rate of methanethiol on the sepiolite-metal complexes was larger than that on the corresponding metal compounds. In the oxidation reaction of methanethiol to dimethyldisulfide in the presence of the sepiolite-metal compound complexes, sepiolite much enhances the catalytic action of metal compounds such as metal chloride and oxalate, and metallophthalocyanine.

Key words: Adsorption, Removal, Methanethiol, Sepiolite, Active carbon, Sepiolite-metal compound complex

INTRODUCTION

Rotten vegetables' odor, foul odor of faeces and exhaust gas from heat diesel engines contain more or less thiols. Particularly, methanethiol is prescribed as one of the offensive odorants in the Offensive Odor Control Law of Japan (Environment Agency of Japan, 1972). So far, methanethiol contained in ambient air has been removed by adsorbent such as active carbon or by oxidation catalysis.

Sepiolite adsorbs various gases in ambient air (Sugiura, Fukumoto and Inagaki, 1991). However, there are few investigations on adsorption of methanethiol on sepiolite in ambient air (Sugiura et al., 1990).

On the other hand, the study on the oxidation mechanism of thiols to disulfides in liquid phase (Tarbell, 1961; Oae, 1982) has clarified that one of the significant reactions of thiols (RSH) is the ready oxidation to disulfide (RSSR). This oxidation can be brought about by mild reagents, such as air or oxygen, and promoted under the influence of various of chemical agents: nickel phthalocyanine (Xan, Wilson, Roberts, and Horton, 1941) and metal compounds having Cu^{2+} , Co^{2+} , Ni^{2+} , etc. in aqueous alkaline solution (Hopton, Swan and Trimm, 1968; Cullis, Hopton, Swan and Trimm, 1968). However,

there are few investigations on the conversion of methanethiol in ambient air into dimethyldisulfide in solid phase.

In this study, the apparent adsorption isotherms of methanethiol for sepiolite and active carbon in ambient air having 60% relative humidity (RH) at 25°C were measured to compare the adsorption of methanethiol on sepiolite with that on active carbon. The removal rates of methanethiol in the air under the influence of various sepiolite-metal compound complexes and simple metal compounds were then measured to discuss the difference in reactivity between these complexes and metal compounds.

EXPERIMENTAL

Materials

Sepiolite was prepared by pulverizing a block-sepiolite into a powder smaller than 44 μm . The block-sepiolite was supplied by Turan Madencilik Sanayi Ticaret Ltd., Turkey. Coconut-shell active carbon (Kintal-BFG, Cataler Industrial Co. Ltd., Japan) in the size smaller than 44 μm was used for comparison (Sugiura, Hayashi and Suzuki, 1991).

Metal compounds such as metal chlorides, oxalates, acetates and metallophthalocyanines (Table 2) were purchased from Nakarai Chemicals Ltds., Wako Pure Chemical Industries, Ltd., and Tokyo Kasei Chemical Industry Co. Ltd., Japan. These compounds were dried at 80°C overnight.

The methanethiol and dimethyldisulfide solutions (both 1 $\mu\text{g}/\mu\text{l}$ -benzene) were obtained from Wako Pure Chemical Industrial, Ltd., Japan and were used as an adsorbate.

Preparation of adsorbents

Sepiolite- $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ complex (or others) was prepared with the following procedure: 0.0075–0.01 mol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 10 g sepiolite and 300 ml water (or ethanol) were mixed in a beaker at 60°C to prepare a sepiolite- $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ complex. The obtained suspension was filtered to gather the precipitate. The precipitate was washed three times with 100 ml deionized water, followed by drying at 80°C overnight. The obtained complex was pulverized and immediately transferred into a desiccator at 25°C, and kept there.

Amount of adsorbed methanethiol: measurement of the concentration

The apparatus for measuring the amount of adsorbed methanethiol consists of four parts; a bag, a vaporizing system, an air-flow meter, and an air-flow pump, which are connected by teflon tubes in series (Sugiura, Hayashi and Suzuki, 1991).

One g of sepiolite was put into the bag. 16, 25, 40, and 50 μl of the methanethiol solution (1 $\mu\text{g}/\mu\text{l}$ -benzene) were introduced with 5 l air having 60% RH at 25°C into the bag. The bag was kept for 5 h in the conditioning chamber controlled at 25°C. During the adsorption process, the concentration of methanethiol in the air was periodically measured, using a gas chromatograph with a flame photometric ionization detector (FPD). The gas chromatographic conditions are described in Table 1.

Each methanethiol solution of the same amount (16, 25, 40, and 50 μl) was vaporized in the bag containing no sepiolite under the same condition, and the original concentration of methanethiol in the air containing no sepiolite was measured, which gives the initial

TABLE 1. Gas Chromatographic Conditions

Stationary phase	25% $\beta\beta'$ -OPTN, Chromosorb W, 4 m, ϕ 3 mm
Column temperature ($^{\circ}$ C)	70
Injection and detector temperature ($^{\circ}$ C)	180
Carrier gas and its flow rate (ml/min)	N ₂ , 60
Sample volume (ml-gas)	1
Detector	FPD

value for the concentration of the system. Then, the initial concentrations of methanethiol in the air were 1.6, 2.5, 4.1 and 5.5 ppms, respectively, for 16, 25, 40 and 50 μ l of the methanethiol solution (1 μ g/ μ l-benzene) introduced into the bag.

The equation of the state of an ideal gas gives the following expression for the amount of methanethiol adsorbed by sepiolite, W (μ mol/g):

$$W = \frac{P_a \cdot V (C_0 - C)}{R \cdot T \cdot w_0} (\mu\text{mol/g}), \quad (1)$$

where P_a , V and T are the pressure [Pa], volume [m^3] and absolute temperature [K] of the air in the bag, respectively, and R is the gas constant, 8.31, [$\text{J} \cdot \text{mol}^{-1} \text{K}^{-1}$]. C_0 and C are the initial and the final concentrations [ppm] of methanethiol. w_0 is the initial weight of the sepiolite [g].

The amount of methanethiol adsorbed by active carbon was calculated by the same way as mentioned above.

Similar experiments were performed for the sepiolite- $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ complex and other complexes with the following typical procedure: 1g of a complex was put into the bag. 50 μ l of the methanethiol solution (1 μ g/ μ l-benzene) was introduced with 10l air of 25 $^{\circ}$ C and 60% RH into the bag. The bag was kept in the conditioning chamber controlled at 25 $^{\circ}$ C. After 5 and 24 h, the concentration of methanethiol in the air was measured. The initial concentration of methanethiol in the air was 2.2 ppm.

The removal rate of methanethiol in the air, RR (%), was given by

$$\text{RR} = \frac{C_0 - C}{C_0} \times 100 (\%). \quad (2)$$

The value of RR under the influence of the sepiolite- $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ complex and other complexes was calculated using the equation (2). These results are summarized in Table 2.

Measurement of gas chromatogram

The gas chromatograms of methanethiol and dimethyldisulfide in the air in the presence of active carbon, sepiolite- $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 and 30wt%) complex, and other sepiolite-metal compound complexes, and those in the air in the absence of adsorbent (having the initial concentration of methanethiol) were measured (Table 1).

The amount of methanethiol in the air, Q_1 (μ mol), was given by

TABLE 2. Removal Rate of Methanethiol*¹⁾ in 101 Air with Various Sepiolite-Metal Compound Complexes and Simple Metal Compounds at 25°C

Adsorbent	Amount of Adsorbent. (g) Sepiolite + Compound	Removal Rate of Methanethiol (Co - C)/Co × 100. (%)	
		After 5h	After 24h
sepiolite-CuCl ₂ ·2H ₂ O complex	0.70 + 0.30	100	100
CuCl ₂ ·2H ₂ O	0 + 0.30	100	100
sepiolite-CuC ₂ O ₄ ·1/2H ₂ O complex	0.87 + 0.13	100	100
CuC ₂ O ₄ ·1/2H ₂ O	0 + 0.13	100	100
sepiolite-Cu(OCOCH ₃) ₂ ·H ₂ O complex	0.85 + 0.15	100	100
Cu(OCOCH ₃) ₂ ·H ₂ O	0 + 0.15	100	100
sepiolite-FeCl ₂ ·4H ₂ O complex	0.87 + 0.13	88	100
FeCl ₂ ·4H ₂ O	0 + 0.13	31	100
sepiolite-FeC ₂ O ₄ ·2H ₂ O complex	0.85 + 0.15	6	23
FeC ₂ O ₄ ·2H ₂ O	0 + 0.15	0	3
sepiolite-CoCl ₂ ·6H ₂ O complex	0.70 + 0.30	57	94
CoCl ₂ ·6H ₂ O	0 + 0.30	2	30
sepiolite-CoC ₂ O ₄ ·2H ₂ O complex	0.87 + 0.13	11	22
CoC ₂ O ₄ ·2H ₂ O	0 + 0.13	3	2
sepiolite-Co(OCOCH ₃) ₂ ·4H ₂ O complex	0.85 + 0.15	7	11
Co(OCOCH ₃) ₂ ·4H ₂ O	0 + 0.15	4	1
sepiolite-NiCl ₂ complex	0.83 + 0.17	14	24
NiCl ₂	0 + 0.17	3	12
sepiolite-C ₃₂ H ₁₆ CuN ₈ complex	0.70 + 0.30	57	100
C ₃₂ H ₁₆ CuN ₈	0 + 0.30	32	88
sepiolite-C ₃₂ H ₁₆ FeN ₈ complex	0.70 + 0.30	100	100
C ₃₂ H ₁₆ FeN ₈	0 + 0.30	99	100
sepiolite-C ₃₂ H ₁₆ CoN ₈ complex	0.70 + 0.30	100	100
C ₃₂ H ₁₆ CoN ₈	0 + 0.30	93	100
Sepiolite	1.00 + 0	11	13

* 1:2.2 ppm of methanethiol.

$$Q_1 = \frac{P_a \cdot V(C_0 - C)}{R \cdot T} (\mu\text{mol}). \quad (3)$$

The amount of dimethyldisulfide in the air, Q_2 (μmol), was given by

$$Q_2 = \frac{P_a \cdot V \cdot C_d}{R \cdot T} (\mu\text{mol}), \quad (4)$$

where C_d is the concentration of dimethyldisulfide in the air.

RESULTS AND DISCUSSION

Methanethiol adsorption on sepiolite and active carbon

Figure 1 shows the typical variation of methanethiol concentration with time, in the air having 60% RH at 25°C. As shown in this figure, the adsorption behavior of sepiolite is remarkably different from that of active carbon. Methanethiol concentration decreases with time in the presence of sepiolite, followed by a saturation with the concentration being not so small. However, it becomes almost zero in the presence of active carbon.

Figure 2 shows the amount of methanethiol adsorbed by sepiolite and active carbon as a function of the equilibrium concentration of methanethiol. As shown in this figure, the adsorption isotherm of sepiolite is remarkably different from that of active carbon. The amount of methanethiol adsorbed by sepiolite increases with its equilibrium concentration. However, the values are as small as $W = 0.12, 0.18, 0.32$ and $0.39 \mu\text{mol/g}$, at $C = 1.0, 1.6, 2.5$ and 3.6 ppm , respectively. The surface of the sepiolite exposed to the air having 60% RH at 25°C would be uniformly covered with water molecules (Sugiura, Hayashi and Suzuki, 1991). The solubility of methanethiol in water is as small as about $0.048 \text{ mol}/100 \text{ g-water}$ (The Merck Index, 1968). Therefore, the small value of the adsorption by the sepiolite would be resulted from low methanethiol solving capacity of the water covering the sepiolite. On the other hand, the amounts of methanethiol adsorbed by active carbon are

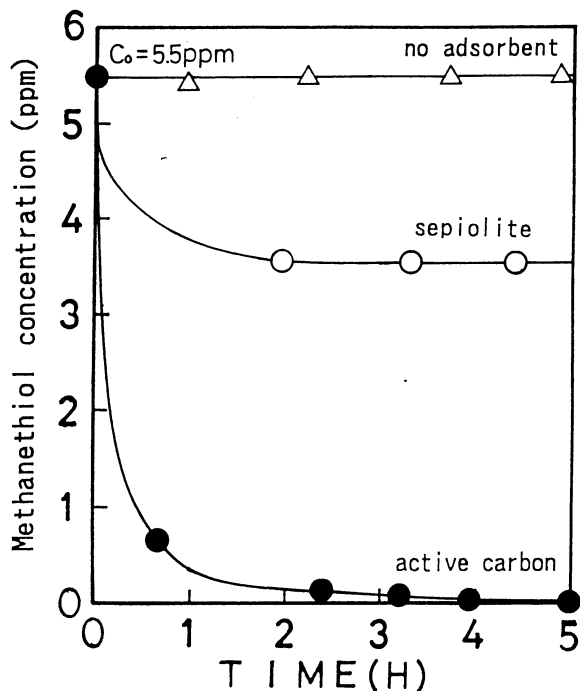


FIG. 1. Typical variations of methanethiol concentration with time in ambient air having 60% RH at 25°C.

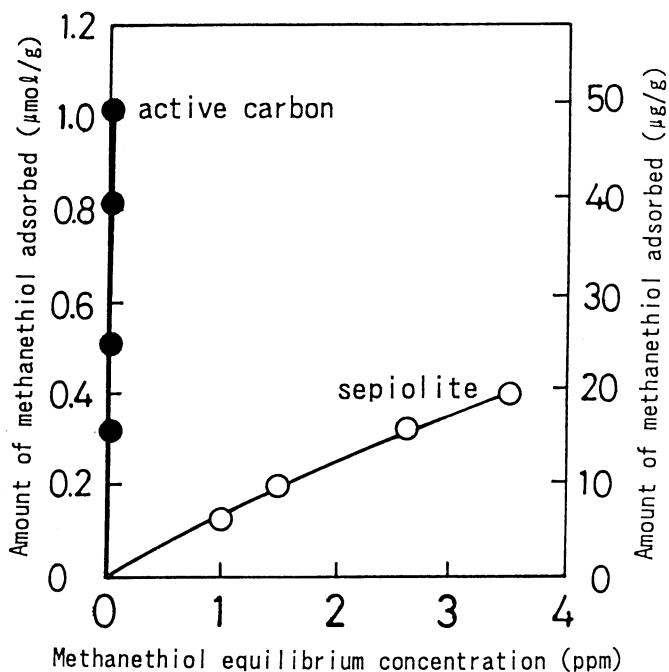


Fig. 2. Apparent methanethiol adsorption isotherm (25°C) of adsorbent in the air having 60% RH.

large as $W = 0.32, 0.51, 0.81$ and $1.1 \mu\text{mol/g}$ at every $C \leq 0.03$ ppm. These amounts correspond to more than 98% of the corresponding initial amounts. These large amounts for active carbon are in contrast to the small amounts for sepiolite. This suggests that almost all methanethiol must be not only adsorbed by active carbon, but also converted to some unknown compound through interaction with active carbon, whose surface is not completely covered with water in the air (Sugiura, Fukumoto and Inagaki, 1991). In the gas chromatogram of the air with methanethiol in the presence of active carbon, methanethiol's peak (retention time: 4.3 min) disappears and a new unknown peak (retention time: 32.1 min) appears in a very small and broad form, whose amount is a trace quantity. The new peak corresponds to the dimethyldisulfide's peak. The process indicates the ready oxidation of thiols (RSH) to disulfide (RSSR):



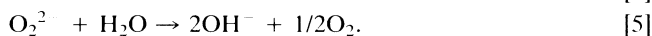
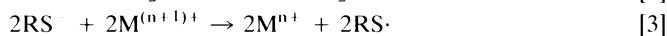
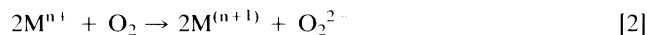
The oxidation can be brought about by mild reagents, such as air or oxygen and by variety of chemical agents; the reaction can usually be stopped at the disulfide stage (Farbell, 1961; Oae, 1982). Therefore, two methanethiol molecules are thought to be converted to one dimethyldisulfide molecule in the air under the influence of active carbon. For the conversion of the thiol to the disulfide, the presence of the strong alkali ion such as K ion, may be responsible, whose effect on the conversion has been studied (Wallace and

Schriesheim, 1965), as the impurity in active carbon (Sugiura and Fukumoto, 1992). On the other hand, the oxidation of methanethiol by sepiolite would be small because of the absence of the strong alkali ion such as K ion and besides because of the fact that the surface of sepiolite is covered with water.

Removal rate of methanethiol under the influence of sepiolite-metal compound complexes and simple metal compounds

Table 2 shows the removal rates of methanethiol in the air having 60% RH at 25°C in the presence of various sepiolite-metal compound complexes, simple metal compounds and sepiolite. As shown in the table, the removal rate value of methanethiol in the air with sepiolite-metal compound complexes was larger than that with the corresponding metal compounds. This shows that sepiolite promotes the catalytic action of metal compound.

A general mechanism for the production of disulphides from thiols in aqueous solution in the transition metal catalysts has been suggested (Wallace, Schriesheim and Jonassen, 1963):



By considering the mechanism [2]–[5] in ambient air, it would be easy to understand the enhancement of the reaction [1] in the presence of the sepiolite-metal compound complex by comparison with that of metal compound. As the sepiolite surface would be uniformly covered with water molecules (Sugiura, Hayashi and Suzuki, 1991), metal ions would be spread widely on the sepiolite surface in the sepiolite-metal compound complex. Therefore, the oxidation-reduction mechanism involving the metal ions on the sepiolite surface would occur easier according to the reactions [2] and [3] than that on the bulky metal compound.

Particularly, in the presence of copper compound such as chloride, oxalate, and acetate, and these corresponding sepiolite-copper compound complexes, the removal rate value of methanethiol is almost 100%, which implies that the oxidation-reduction mechanism involving the copper ion would occur easiest among transitional metal ions (Hopton, Swan and Trium, 1968).

Next, the gas chromatogram of the air with methanethiol in the presence of sepiolite-CuCl₂·2H₂O complex was studied. The result is given in Fig. 3. As shown in the figure, in the air with methanethiol in the presence of sepiolite-CuCl₂·2H₂O complex, dimethyl-disulfide (retention time: 32.2 min) appears as a broad peak. This means that the reaction [1] can be brought about by this adsorbent as well as active carbon as previously described.

Figure 4 shows the methanethiol and dimethyl-disulfide concentrations plotted as a function of time under the influence of the sepiolite-CuCl₂·2H₂O complex after exposure to methanethiol in the air. As shown in the figure, after 1.5 h, the methanethiol concentration reaches zero, while the dimethyl-disulfide concentration increases with time to reach saturation. If methanethiol is completely converted into gaseous dimethyl-disulfide on the surface of the sepiolite-CuCl₂·2H₂O complex after 100 min, the value of Q₁ is twice

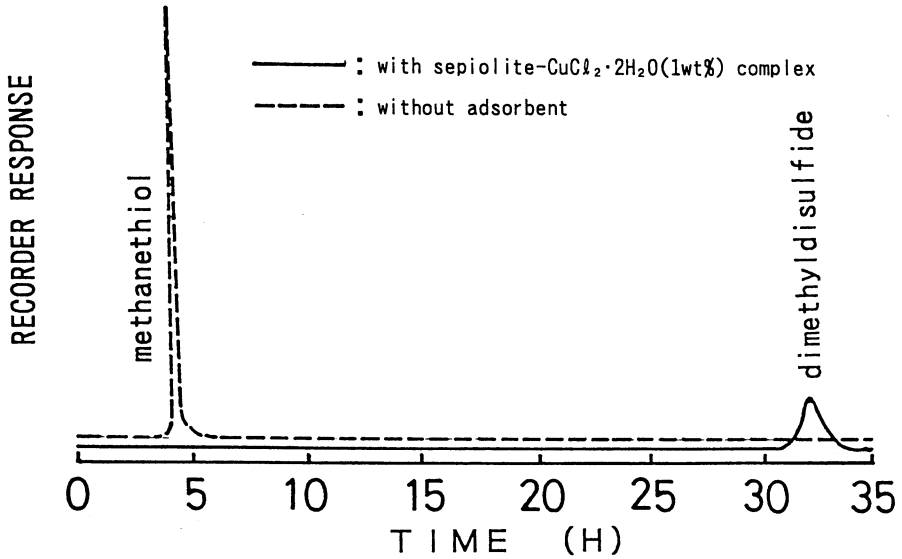


FIG. 3. Gas chromatogram

50 μ l of the methanethiol solution (1 μ l/ μ g-benzene) was vaporized in 5l air in the bag (a) with the sepiolite-CuCl₂·2H₂O (30wt%) complex and (b) without adsorbent. The methanethiol concentration in the air was measured after 2.5 h.

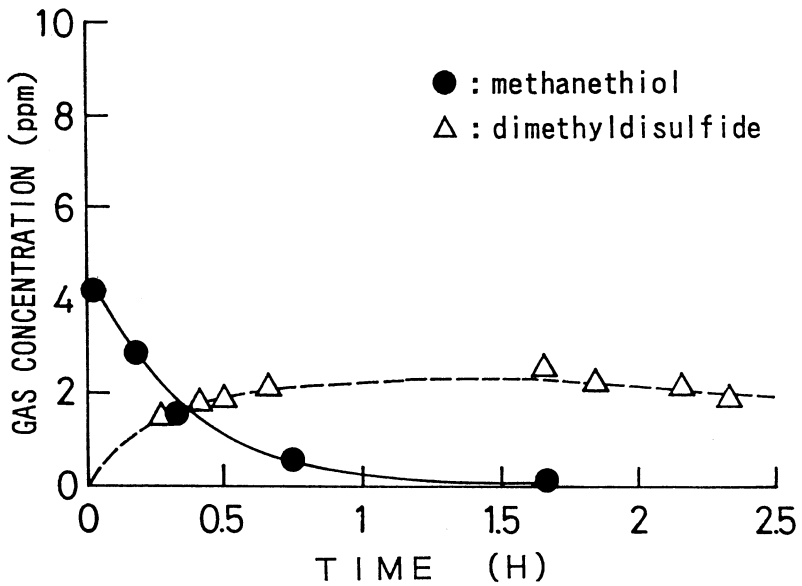


FIG. 4. Methanethiol and dimethyl disulfide concentrations plotted as a function of time, under the influence of the sepiolite-CuCl₂·2H₂O (1wt%) complex. The initial methanethiol concentration is 10.03 ppm in 5l air. The sepiolite-CuCl₂·2H₂O (1wt%) complex used is 3g.

times as large as that of Q_2 ($Q_2 = 0.5Q_1$) through the reaction [1]. Here, the amount of methanethiol consumed, Q_1 , is $2.10 \mu\text{mol}$ ($C = 0 \text{ ppm}$, $C_0 = 10.03 \text{ ppm}$) at 100 min, while the amount of dimethyldisulfide formed, Q_2 , is $0.52 \mu\text{mol}$ ($C_d = 2.55 \text{ ppm}$) at 100 min ($Q_2 \approx 0.25Q_1$). This result indicates that the formed dimethyldisulfide is thought to be further converted into some unknown complex connected with the surface of the sepiolite- $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ complex.

CONCLUSION

- 1) In ambient air having 60% RH at 25°C , the amount of methanethiol adsorbed on sepiolite was very small. On the other hand, the removal rate of methanethiol in the presence of coconut-shell active carbon was very large. Methanethiol would be converted into dimethyldisulfide under the influence of the strong alkali ion in active carbon.
- 2) The removal rate of methanethiol on the sepiolite-metal compound complexes in the air was larger than that on the corresponding metal compounds.
- 3) In the oxidation reaction of methanethiol to dimethyldisulfide in the presence of the sepiolite-metal compound complexes, sepiolite much enhances the catalytic action of metal compounds such as metal chloride and oxalate, and metallophthalocyanine.
- 4) Methanethiol was completely ($\approx 100\%$) removed by $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuC}_2\text{O}_4 \cdot 1/2\text{H}_2\text{O}$, and $\text{Cu}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ and the corresponding sepiolite-copper compound complexes.

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