The catalytic incineration of $(CH_3)_2S$ and its mixture with CH_3SH over a Pt/Al_2O_3 catalyst

H. Chu*, W.T. Lee, K.H. Horng, T.K. Tseng

*Department of Environmental Engineering, National Cheng Kung University,
1 University Road, Tainan 70101, Taiwan*

Abstract

Catalytic incineration is one of the cost-effective technologies to solve the troublesome volatile organic compounds (VOCs). However, some sulfur containing VOCs, such as dimethyl sulfide, may deactivate the Pt catalyst that is commonly used in the catalytic incineration process. This paper provides information on the poisoning effect of $(CH_3)_2S$. The catalytic incineration of $(CH_3)_2S$, typically emitted from the petrochemical industry, over a Pt/Al_2O_3 fixed bed catalytic reactor was studied. The effects of operating parameters including inlet temperature, space velocity, $(CH_3)_2S$ concentration, O_2 concentration and catalyst size were characterized. Catalytic incineration on a mixture of $(CH_3)_2S$ with CH_3SH was also tested. The results show that the conversions of $(CH_3)_2S$ increase as the inlet temperature increases and the space velocity decreases. The higher the $(CH_3)_2S$ concentration is, the lower its conversion is. The O_2 concentration has a positive effect on the conversion of $(CH_3)_2S$. $(CH_3)_2S$ has a poisoning effect on the Pt/Al_2O_3 catalyst, especially at lower temperatures. The conversion of $(CH_3)_2S$ is significantly suppressed by the existence of CH_3SH. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic incineration; Pt/Al_2O_3; Dimethyl sulfide; Methyl mercaptan; Poisoning

1. Introduction

Volatile organic compounds (VOCs) are defined as the organic compounds that have high vapor pressure and are easily vaporized at the condition of ambient temperature and pressure. Many hydrocarbons, including nitrogenous, chlorinated, and sulfurated organics are determined to be VOCs. These compounds are usually found in the industries that manufacture or utilize organic solvents, e.g. petrochemical, pulp, or coating industry. Besides causing harmful effects on human organs, many VOCs may also react with NO_x in the

---

* Corresponding author. Tel.: +886-6-208-108; fax: +886-6-275-2790.
E-mail address: chuhsin@mail.ncku.edu.tw (H. Chu).

atmosphere to form photochemical smog and O_3 [1]. Some VOCs such as mercaptans, dimethyl sulfides, or amines, are not extremely toxic but may present offensive odor even at extremely low concentration. In order to remove these troublesome substances, a number of technologies have been developed. Among them, catalytic incineration has been paid the most attention lately because it is a final disposal and energy saving process [2,3]. However, sulfur-containing VOCs may deactivate the catalyst and reduce the advantage of catalytic incineration. The major parameters affecting catalytic incineration of VOCs include catalyst types, VOC types, VOC concentration, operating temperature, space velocity and O_2 concentration [4]. Catalysts can be divided into two categories: precious metals and metal oxides. Heyes et al. evaluated a series of catalysts for the destructive oxidation of *n*-butanal and methyl mercaptan. They found that the ability to destroy butanal in mixtures with methyl mercaptan at the end of life-tests, decreased in the following order: $CuO = Pt > MnO_2 > V_2O_5 > CO_3O_4$. Their study revealed that the catalyst type was a key parameter for catalytic incineration [5]. Tichenor and Palazzolo did a series of tests on catalytic incineration of tens of VOCs using precious metals. They found that destructibility of VOCs using precious metals decreased in the following order: alcohols > cellusolves > aldehydes > aromatics > ketones > acetates > alkanes > chlorinated hydrocarbons [6]. However, the different behaviors of the catalytic conversion of single VOC and the VOC in a mixture of VOCs have not been thoroughly studied. In general, the operating temperature of catalytic incineration depends on catalyst types, VOC types, concentration of VOCs and space velocity. From the definition, space velocity is the inverse of residence time of VOCs in the catalytic reactor. Therefore, residence time would decrease as space velocity increases and the conversion of VOCs would drop. Völter et al. indicated that the activity of a Pt catalyst was stronger in air than in pure oxygen [7]. Ross and Sood used $CoMo_4 \cdot H_2O$ to control a simulated pulp mill effluent gas containing methyl mercaptan, while O_2 concentrations varied from 1 to 4%. They found that the activity of the catalyst with respect to the production of an intermediate-dimethyl disulfide fell as the O_2 concentration in the effluent increased from 1 to 4%, while the production of SO_2, the complete oxidation product of methyl mercaptan, simultaneously increased [8].

Chu and Lee used a Pt/Al_2O_3 catalyst to catalytically convert ethanol in mixtures with dimethyl disulfide. They found that the conversion of ethanol was significantly suppressed by the existence of $(CH_3)_2S_2$ at temperature lower than 300°C [9]. Jennings et al. showed that S was a reversible inhibitor to the catalyst. Its effects depended on the S content of the VOCs and operating temperature [10]. Pope et al. used a Pt catalyst to catalytically convert *n*-butanal in mixtures with methyl mercaptan. They found that the conversion of *n*-butanal was suppressed by CH_3SH if the operating temperature was below 300°C [11]. A number of earlier studies on the catalytic conversion of CO with mixtures of $(CH_3)_2S$ using various types of Co_3O_4 catalyst were investigated by Pope et al. They suggested that the higher the specific surface area of the catalyst was, the more sites could be covered by sulfur and the catalyst's sulfur-resistibility was higher [12].

This study was carried out by catalytic incineration of dimethyl sulfide, typically emitted from the petrochemical industry, over a Pt/Al_2O_3 fixed bed reactor. The effects of operating parameters, including inlet temperature, space velocity, $(CH_3)_2S$ concentration, O_2 concentration and catalyst size were characterized. A life test of the catalyst on $(CH_3)_2S$ was performed to identify the sulfur poisoning effect. Catalytic incineration on a mixture

of $(CH_3)_2S$ with CH_3SH was also tested to determine the interferences of CH_3SH on the performance of $(CH_3)_2S$ conversion.

2. Materials and methods

The catalytic incineration of this study was done in a bench scale fixed bed reaction system. The system can be divided into three parts: an effluent gas simulation system, a catalytic incineration system and a combustion gas analyzing system as shown in Fig. 1. The effluent gas simulation system was composed of an air compressor (SWAN, 1/4 hp), a N_2 cylinder (99.9%, San Fu), four mass flow meters (Teledyne Hasting-Raydist, HFC-202), two plug-flow mixers (Omega, FMX7106), a water bath (Deng Yng, $-20°C$ to $80°C$) and two VOC vapor generators (Pyrex). Flow rates of dilution N_2, purge N_2 and dilution air were controlled by three mass flow meters, to prepare the desired $(CH_3)_2S$ and O_2 concentrations. Simulated gas of CH_3SH was made of CH_3SH cylinder gas (Merck Chemicals, >99.5%), dilution N_2 and dilution air. The simulated gas was then preheated by an electrical heating tape before going through the reactor. The material of pipings, valves, regulators or fittings used was either SS-316 or Teflon. The catalytic incineration system was composed of a
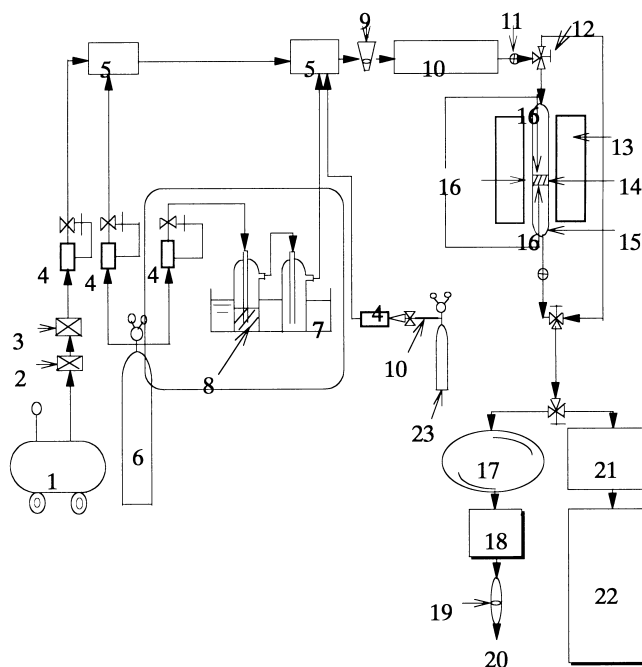

Fig. 1. A schematic diagram of a bench-scale catalytic incinerator (1: air compressor; 2: filter; 3: dryer; 4: mass flow meter; 5: mixer; 6: N_2; 7: water bath; 8: liquid VOCs; 9: rotameter; 10: preheater; 11: sampling port; 12: three way valve; 13: heater; 14: catalyst; 15: reactor; 16: thermocouple; 17: autosampling valve; 18: GC-FID/FPD; 19: bubble meter; 20: vent; 21: sampling system; 22: analyzers SO_2, O_2, CO, CO_2 and 23: methyl mercaptan).

Table 1
The basic properties of NIKKI NS-10 catalyst

Catalyst	Shape	Size (mm)	Bulk density (g/ml)	Pt content (g/l)
Pt/Al_2O_3	Pellet	3–3.5	0.35–0.4	1.8

custom-made SS-316 tube reactor and an electrical heater. The length, internal diameter and outer diameter of the reactor were 45, 1.5 and 2.0 cm, respectively. A 200 mesh SS-316 sieve was set in the reactor, 24 cm below the top of the tube, to support the catalyst. The thickness of catalyst packing was 1 cm. A thin layer of glass fiber and a layer of glass bead with a 2-mm diameter also covered the catalyst packing to uniformly distribute the gas. Two K type thermocouples were inserted into the reactor to the positions on the top and bottom of the catalyst packing, respectively, to measure and control the inlet and outlet temperature. The gas analyzing system was composed of a GC unit (Shimadzu, GC-14B) and four combustion gas analyzers: SO_2 analyzer (Milton Roy Model ZRF infrared analyzer), O_2 analyzer (Signal Model magneto dynamic type), CO analyzer (Signal Series 2000) and CO_2 analyzer (Signal Series 2000). The GC column was a 30 m long capillary column with a diameter of 0.53 mm (J and W Scientific #115-3432). A 1:1 splitter was connected with the column to split the sample gas into FID and FPD detectors. An icebox impingement condenser (Pyrex) and two particle filters (Balston, 95S6 and 45G) were installed between
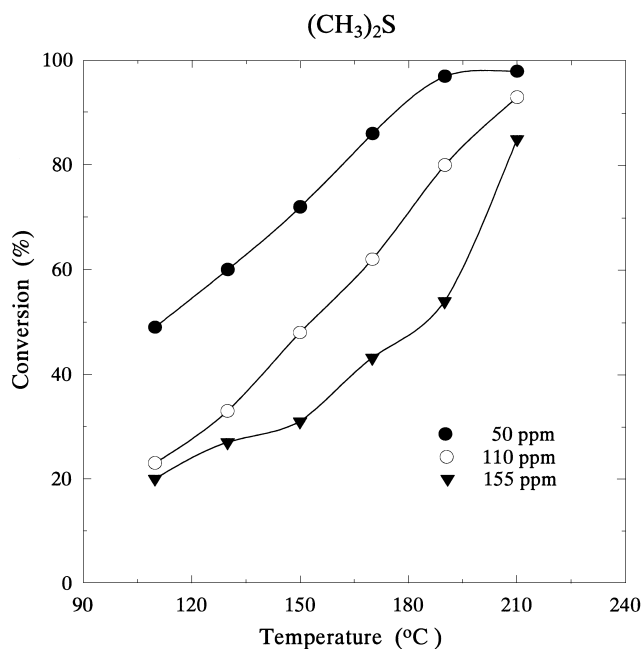

Fig. 2. The effect of $(CH_3)_2S$ concentration on the catalytic conversion of $(CH_3)_2S$ (space velocity: 55,000 h^{-1}, O_2 concentration: 20.8%).

the sampling port and four combustion gas analyzers. This arrangement was designed to prevent the analyzers from damage by condensed water and particles. All mass flow meters and rotameters used in this study were calibrated by a bubble meter (Humonic digitial flow meter 650) or a dry gas meter (Shinagawa DK-SCF-T) at their proper ranges. Standard gases included zero gas (N_2, 99.995%, San Fu), SO_2 span gas (435 ppm, SanFu), O_2 span gas (19%, San Fu), CO span gas (502 ppm, San Fu), CO_2 span gas (1970 ppm, San Fu), CH_3SH span gas (200 ppm, U S Gas) and $(CH_3)_2S$ span gas (200 ppm, U S Gas). The catalyst samples were taken before and after the reaction to determine the changes of their specific surface area, because of sulfur poisoning, by a BET specific surface area analyzer (FlowSorb II 2300), to determine the Changes of their sulfur content by an ESCA analyzer (VG ESCA 210) and to determine the changes of their crystalloid by a XRD analyzer (Rigaku D/MAX III). Liquid $(CH_3)_2S$ was a product of Merck Chemical Inc. (purity >99%). The catalyst was a commercial product of NIKKI NS-10 Pt/Al_2O_3. Its basic properties are shown in Table 1.

The experiments were also divided into three parts. The first part was performed to investigate the performance of Pt/Al_2O_3 on catalytic conversion of $(CH_3)_2S$. The operating parameters and ranges were inlet temperature (110–400°C), $(CH_3)_2S$ concentration (50–190 ppm), space velocity (30,000–80,000 h^{-1}) and O_2 concentration (1–20.8%). The second part was a life test of the catalyst by catalytic incineration of $(CH_3)_2S$ to identify the sulfur poisoning effect. The last part was conducted to catalytically incinerate a mixture of $(CH_3)_2S$ with CH_3SH. The results could be compared with the first part of the experiments
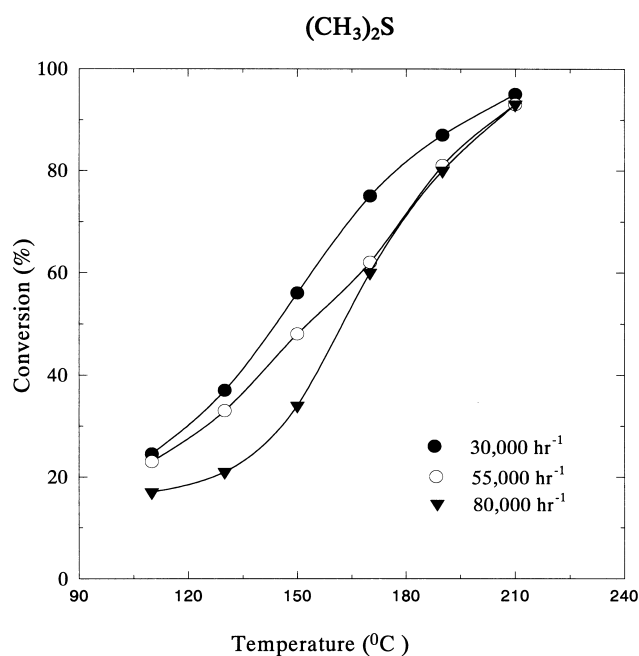

Fig. 3. The effect of space velocity on the catalytic conversion of $(CH_3)_2S$ ($(CH_3)_2S$ concentration: 110 ppm, O_2 concentration: 20.8%).

to determine the interference of $(CH_3)_2S$ conversion by adding CH_3SH. Reagent grade liquid dimethyl sulfide was injected into the VOC generator, which was kept at a constant temperature of $-5°C$ in the water bath. Purged N_2 carried the vaporized VOC to mix with dilution air and N_2 in the mixture to simulate the waste gas from a typical petrochemical plant, at a certain flow rate and O_2 concentration. The simulated gas was injected into the catalytic reactor heated by an electrical furnace. Gas samples (1 ml) were taken before and after the reaction, by an on-line autosampler, to be injected into the GC to determine the conversion of the VOC. The gas samples before and after the reaction were also analyzed by four gas analyzers to determine the extent of complete oxidation.

3. Results and discussion

The preliminary tests started from a series of blank tests by replacing catalyst packing with glass fiber. The results show that the conversion of $(CH_3)_2S$ without catalyst is low in the operating ranges of this study. This suggested that the catalyst is the key element for the conversion of $(CH_3)_2S$. The commercial Pt catalyst was ground to three particle size ranges: 30–50 mesh, 50–100 mesh and 100–200 mesh. Their specific surface areas remain the same as that of the raw catalyst. A series of tests were performed on conversion of $(CH_3)_2S$ over three types of catalyst with different sizes. The results show that the performances of the
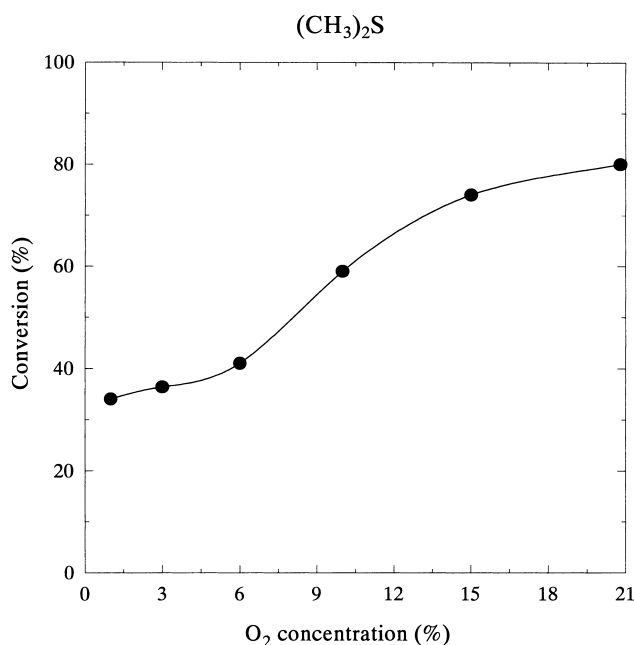

Fig. 4. The effect of O_2 concentration on the catalytic conversion of $(CH_3)_2S$ (inlet temperature: 190°C, $(CH_3)_2S$ concentration: 110 ppm, space velocity: 55,000 h^{-1}).
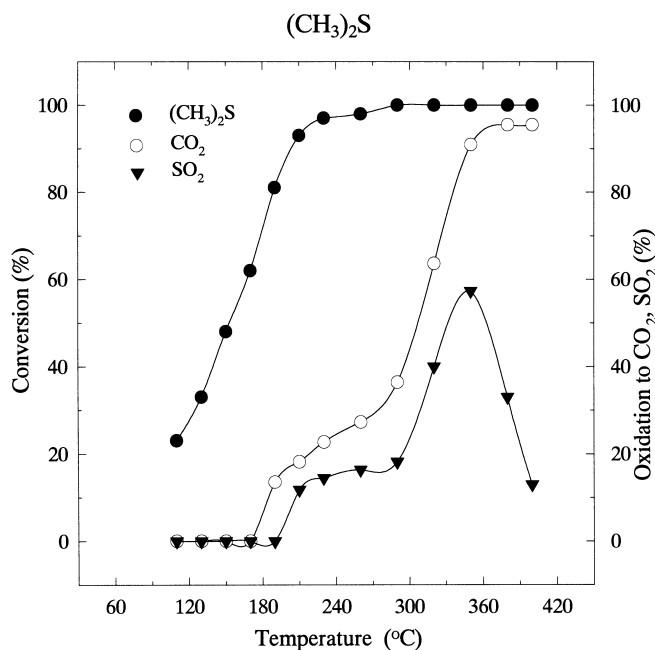
(CH$_3$)$_2$S

Fig. 5. The relationship of (CH$_3$)$_2$S conversion, CO$_2$ yield and SO$_2$ yield at various temperatures ((CH$_3$)$_2$S concentration: 110 ppm, space velocity: 55,000 h^{-1}, O$_2$ concentration: 20.8%).

catalyst with different sizes were not significantly different from one another. Therefore, we chose the catalyst with size of 50–100 mesh to carry out the experiments for the rest of this study, in order to reduce both the mass transfer limitation and grinding effort.

The effect of (CH$_3$)$_2$S concentration on its conversion at various temperatures is shown in Fig. 2. It suggests that the conversion of (CH$_3$)$_2$S increases as inlet temperature increases in the range of 110–210°C. It also can be found that the conversion of (CH$_3$)$_2$S increases as its concentration decreases from 155 to 50 ppm. Fig. 3 shows that the lower the space velocity is, the higher the conversion of (CH$_3$)$_2$S is. The effect of O$_2$ concentration on the conversion of (CH$_3$)$_2$S at a temperature of 270°C is shown in Fig. 4. We find that the conversion of (CH$_3$)$_2$S increases as O$_2$ concentration increases. This is consistent with the results of Ross and Sood [8] and Chu and Horng [13], in which the results showed that the adsorption of the O$_2$ molecule is important in the process of catalytic incineration of CH$_3$SH and (CH$_3$)$_2$S as described by the Langmuir–Hinshelwood model for the catalytic incineration of CH$_3$SH and (CH$_3$)$_2$S. Chu and Wu [14] also showed that the O$_2$ concentration had a positive effect on the conversion of ethyl mercaptan. Fig. 5 shows that the conversion of (CH$_3$)$_2$S reaches 97% around 230°C, but the CO$_2$ yield only reaches about 20% at the same temperature. This suggests that the (CH$_3$)$_2$S intermediates of the reaction are the major components of the oxidized gas at lower temperatures. Essentially complete oxidation of (CH$_3$)$_2$S to CO$_2$ is not reached until the operating temperature is more than 380°C. At 380°C, the CO$_2$ yield is 96%. The yield of SO$_2$, another complete oxidation product, shows a wave pattern within
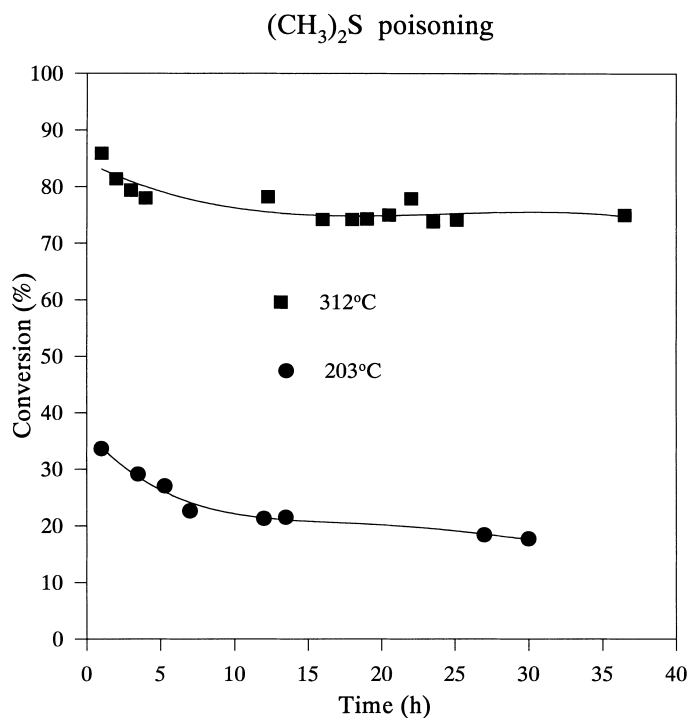
$(CH_3)_2S$ poisoning

Fig. 6. The poisoning effect of $(CH_3)_2S$ on the Pt/Al_2O_3 catalyst (inlet temperatures: 312 and 203°C, $(CH_3)_2S$ concentration: 160 ppm, space velocity: 55,000 h^{-1}, O_2 concentration: 20.8%).

the temperature range tested in this study. The peak of SO_2 yield of this study, with a value of 60%, happened around 350°C. This result is consistent with the results of Heyes et al. and Pope et al. [5,11]. Besides the sulfur containing VOC intermediates that may be formed at low temperatures, the other reasons for S not being balanced at high temperatures may be due to the possible formation of SO_3 and SO_4^{2-}.

A series of life-tests of the catalyst under the condition of 160 ppm $(CH_3)_2S$ were conducted to identify the sulfur poisoning effect and the results are shown in Fig. 6. The performance of the catalyst declines dramatically for a while, and then reaches a stable condition. This phenomenon may be due to the possibility that certain activated sites of the catalyst would form irreversible sulfur-poisoned sites with sulfur, that would need time to accomplish the irreversible reaction. The remaining sites of the catalyst could be reversible sulfur-poisoned sites. Fig. 7 shows that the BET (Brunauer–Emmett–Teller method) specific surface area of the poisoned catalyst is less than that of the fresh catalyst. This also suggests that some of the catalyst surface may be covered by sulfur compounds after the reaction. This is consistent with the results of Chu and Lee [9], in which the results showed that the $(CH_3)_2S_2$ had a poisoning effect on the Pt/Al_2O_3 catalyst. An X-ray diffraction examination on the fresh catalyst and the poisoned catalyst was conducted in this study. The results are shown in Fig. 8. The ordinate is the intensity of the diffraction and the abscissa
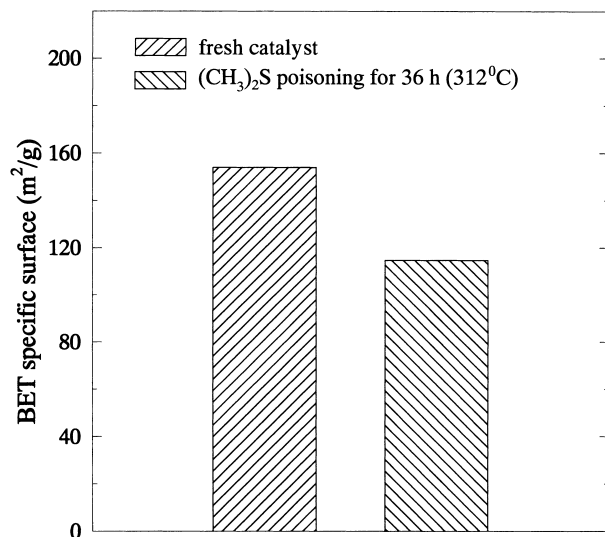
Fig. 7. The changes of specific surface area of the Pt/Al$_2$O$_3$ catalyst after sulfur poisoning.

is the X-ray detecting angle. The solid triangles represent the Al$_2$O$_3$ crystalloids and the hollow triangles represent the Pt crystalloids. The X-ray diffraction pattern differences of both catalysts are not significant. It suggests that the crystalloid of activated sites of the catalyst may not change at all. An electron spectroscopy for chemical analysis (ESCA) on the fresh catalyst and the poisoned catalyst, incinerating with 150 ppm CH$_3$SH at 315°C, 20.8% O$_2$ and 50,000 h^{-1} for 32 h, was conducted in this study. The results show that the
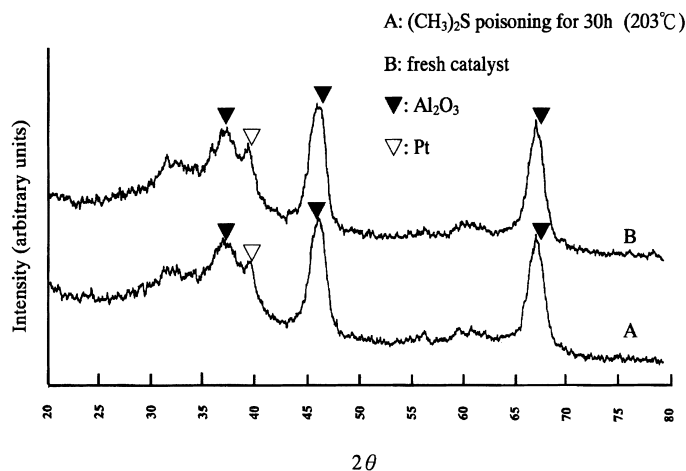

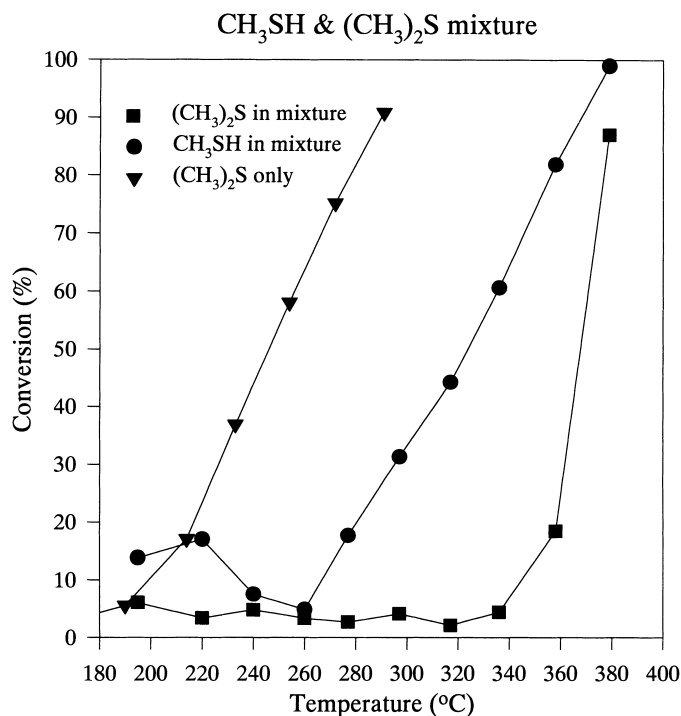Fig. 8. The changes of crystalloid of the Pt/Al$_2$O$_3$ catalyst after catalytic incineration of (CH$_3$)$_2$S.

CH₃SH & (CH₃)₂S mixture

Fig. 9. The differences between the catalytic conversion of $(CH_3)_2S$ and $(CH_3)_2S/CH_3SH$ mixture ($(CH_3)_2S$ concentration: 140 ppm, CH_3SH concentration: 94 ppm, space velocity: 80,000 h^{-1}, O_2 concentration: 20.8%).

sulfur contents on the surface of the fresh catalyst and the poisoned catalyst are 0.2 and 2.8%, respectively. Therefore, it confirms that the catalyst surface may be covered by sulfur to form reversible sulfur-poisoned sites only.

For the case of the catalytic incineration of a mixture of $(CH_3)_2S$ and CH_3SH, 94 ppm CH_3SH was added into a 140 ppm $(CH_3)_2S$ simulated gas. In order to compare its effect with the single component case, the operating conditions remained the same for both single component and mixture cases. The results are shown in Fig. 9. The conversion of $(CH_3)_2S$ is suppressed by C_2H_5SH significantly.

4. Conclusions

The catalytic incineration of $(CH_3)_2S$ on a Pt/Al_2O_3 catalyst was conducted over a variety of operating conditions. The results show that the conversion of the $(CH_3)_2S$ increases as the inlet temperature increases and the space velocity decreases. The higher the $(CH_3)_2S$ concentration is, the lower its conversion is. The O_2 concentration has a positive effect on the conversion of $(CH_3)_2S$. $(CH_3)_2S$ has a considerable poisoning effect on the Pt/Al_2O_3 catalyst, especially at lower temperatures. The conversion of $(CH_3)_2S$ is significantly suppressed by the existence of CH_3SH.

Acknowledgements

References

[1] N. de Nevers, Air Pollution Contol Engineering, 2nd Edition, McGraw-Hill, Singapore, 2000, pp. 571–572.

[2] D.R. Van der Vaart, W.M. Vatavuk, A.H. Wehe, J. Air Waste Manage. Assoc. 41 (1) (1991) 92–98.

[3] D.R. Van der Vaart, W.M. Vatavuk, A.H. Wehe, J. Air Waste Manage. Assoc. 41 (4) (1991) 497–501.

[4] J.J. Spivey, Ind. Eng. Chem. Res. 26 (11) (1987) 2165–2180.

[5] C.J. Heyes, J.G. Irwin, H.A. Johnson, R.L. Moss, J. Chem. Tech. Biotechnol. 32 (1982) 1025–1033.

[6] B.A. Tichenor, M.A. Palazzolo, Environ. Prog. 6 (3) (1987) 172–176.

[7] J. Völter, G. Lietz, H. Spindler, H. Lieske, J. Catal. 104 (1987) 375–380.

[8] R.A. Ross, S.P. Sood, Ind. Eng. Chem. Prod. Res. Rew. 16 (2) (1977) 147–150.

[9] H. Chu, W.T. Lee, Sci. Total Environ. 209 (1998) 217–224.

[10] M.S. Jennings, N.E. Krohn, R.S. Berry, M.A. Palazzolo, R.M. Parks, K.K. Fidler, Catalytic Incineration for Control of Volatile Organic Compound Emissions, Noyes Publication, NJ, 1985, pp. 14–22.

[11] D. Pope, D.S. Walker, R.L. Moss, Atmos. Environ. 12 (1978) 1921–1927.

[12] D. Pope, D.S. Walker, R.L. Moss, Atmos. Environ. 10 (1976) 951–956.

[13] H. Chu, K. Horng, Sci. Total Environ. 209 (1998) 149–156.

[14] H. Chu, L.W. Wu, J. Environ. Sci. Health, Part A A33 (6) (1998) 1119–1148.