Laboratory study of poisoning of a MnO/Fe$_2$O$_3$ catalyst by dimethyl sulfide and dimethyl disulfide

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Abstract

The catalytic incineration of dimethyl sulfide and dimethyl disulfide in a MnO/Fe$_2$O$_3$ fixed bed catalytic reactor was studied. This paper provides information on the affect of the operating parameters that included: inlet temperature, space velocity, VOC concentration and O$_2$ concentration. The results show that the conversion of VOCs increases as the inlet temperature increases and the space velocity decreases. The higher the concentration of VOCs, the lower their conversions. The O$_2$ concentration has no affect on the conversion of VOCs. VOCs have poisoning affects on the MnO/Fe$_2$O$_3$ catalyst, especially at lower temperatures.
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Keywords: Catalytic incineration; MnO/Fe$_2$O$_3$; Dimethyl sulfide; Dimethyl disulfide; Sulfur poisoning

1. Introduction

Volatile organic compounds (VOCs) have high vapor pressures and are easily vaporized at ambient temperature and pressure. Most hydrocarbons, including nitrogenous, chlorinated, and sulfurated organics are VOCs. These compounds are usually found in the industries that manufacture or utilize organic solvents, e.g. petrochemical, pulp, or coating industry. Besides being toxic, VOCs may react with NO$_x$ in the atmosphere to form even more toxic photochemical smog and O$_3$. Some VOCs, such as mercaptans, dimethyl sulfides, or amines, are not extremely toxic themselves but may have offensive odors even at extremely low concentrations.

The common process utilized for control of chlorinated hydrocarbons is thermal incineration. This process requires extremely high temperatures approaching 1000 °C [1]. While

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incineration is a simple and often effective method of control, the high temperature requires much fuel. Moreover, there is little control over the ultimate oxidation products.

An alternate method of eliminating VOCs in waste streams is heterogeneous catalytic incineration [2]. That process has received much attention lately because it is not energy intensive [3,4]. However, sulfur-containing VOCs may deactivate the catalyst.

The major variable affecting catalytic incineration of VOCs include catalyst type, VOC species, VOC concentration, operating temperature, space velocity and O_2 concentration. Catalysts reported having destructive oxidation of VOCs consist mostly of base metal oxides and noble metals on acidic supports [5–7]. Wang and Weng [8] indicated that Mo not only promotes the activity of $CuO/\gamma\text{-}Al_2O_3$ for the oxidative decomposition of $(CH_3)_2S_2$, but also enhances resistance to deactivation by sulfur compounds. The effect of sulfur on deactivation of palladium catalysts for methane oxidation has been investigated [9]. The results show that the catalyst activity decreases with increased H_2S deposition and increased temperature from 100 to 400 °C. Chang and Chang [10] studied the affect of sulfur poisoning and hydrogen reaction for tetralin hydrogenation over $\gamma\text{-}Al_2O_3$ supported Pt catalyst. They reported that the decline of the reaction rate is caused by the formation of PtS, the adsorption of H_2S on the active site, and the agglomeration of Pt particles.
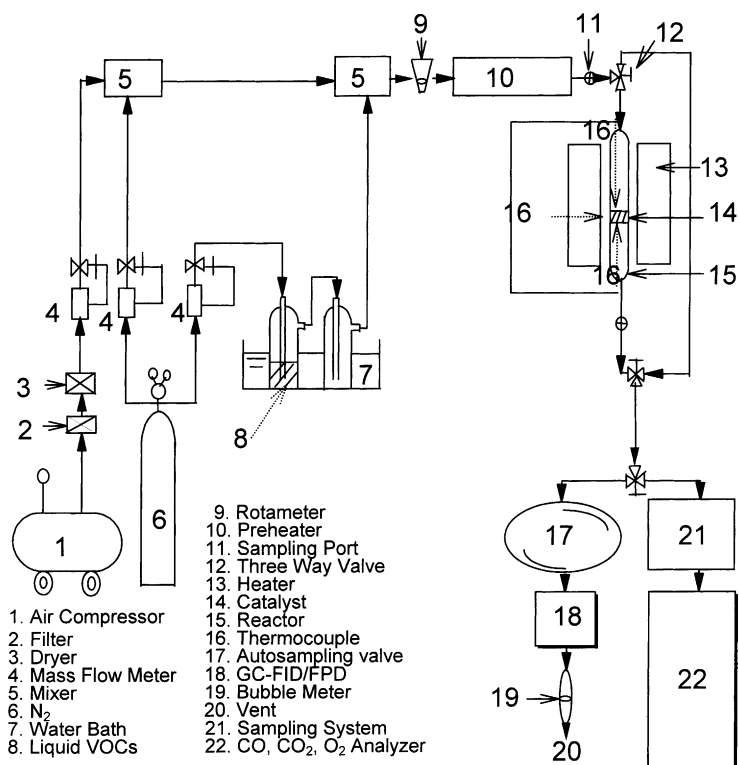

9. Rotameter
10. Preheater
11. Sampling Port
12. Three Way Valve
13. Heater
14. Catalyst
15. Reactor
16. Thermocouple
17. Autosampling valve
18. GC-FID/FPD
19. Bubble Meter
20. Vent
21. Sampling System
22. CO, CO_2, O_2 Analyzer

1. Air Compressor
2. Filter
3. Dryer
4. Mass Flow Meter
5. Mixer
6. N_2
7. Water Bath
8. Liquid VOCs

Fig. 1. Schematic diagram of bench-scale catalytic incinerator.

Table 1
The basic properties of NISSAN GIRDLER G-34 and N-150 catalysts

Model	Catalyst	Support	Shape	Size	Bulk density
G-34	Cr_2O_3 (7%)	Al_2O_3	Rhomboid	2 cm (W) $\times$ 2 cm (H)	–
N-150	MnO (30%)	Fe_2O_3	Cylinder	6 mm (D) $\times$ 6 mm (H)	2.2 g/ml

Jennings et al. [13] showed that sulfur was a reversible catalyst inhibitor [11]. That effect depended on the S content of VOCs and operating temperature. Pope et al. [14] used a Pt catalyst to convert n-butanal in a mixture with methyl mercaptan [12]. They found that the conversion of n-butanal was suppressed by CH_3SH if the operating temperature was below 300 °C.

A study of the catalytic conversion of CO with mixtures of $(CH_3)_2S$ using various types of Co_3O_4 catalyst was conducted by Pope et al. [14,15]. They suggested that as higher the
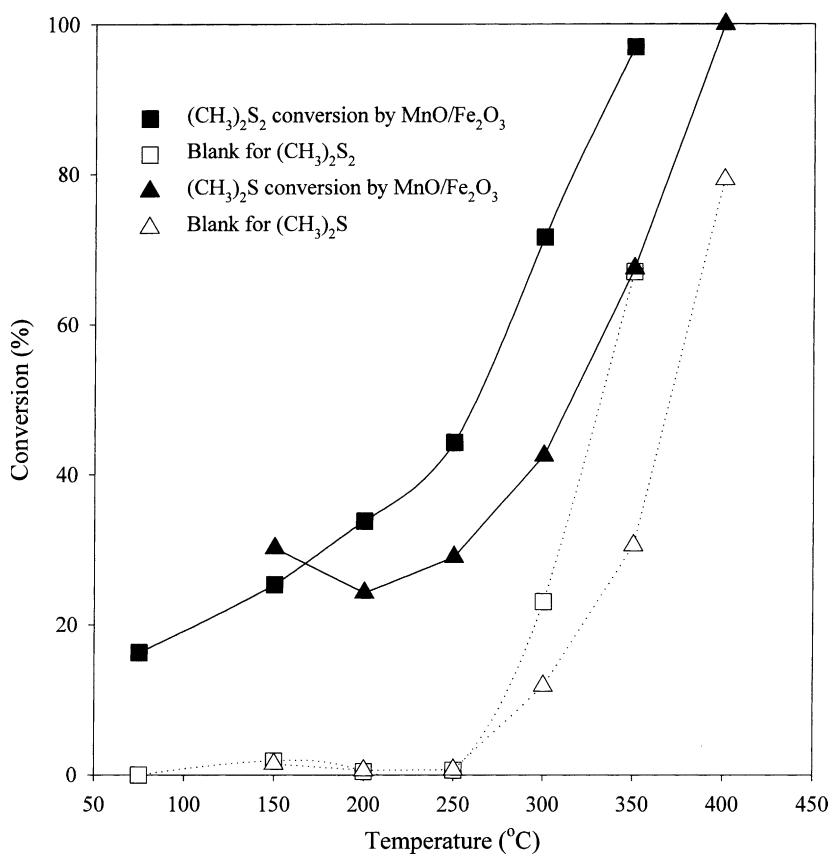

Fig. 2. Comparisons of the catalytic incineration of $(CH_3)_2S$ on MnO/Fe_2O_3 catalyst and Cr_2O_3/Al_2O_3 catalyst at various temperatures ($(CH_3)_2S$ concentration: 100 ppm; space velocity: 55,000 h^{-1}; O_2 concentration: 20.8%).

specific surface area of the catalyst was, more sites could be utilized by the sulfur and the catalyst's sulfur-resistance was higher. Chu and Lee [16] used a Pt/Al$_2$O$_3$ catalyst to convert ethanol in mixtures with dimethyl disulfide. They found that the conversion of ethanol was significantly suppressed by the existence of (CH$_3$)$_2$S$_2$ at temperatures lower than 300 °C. Chu et al. [17] used a MnO/Fe$_2$O$_3$ catalyst to study the kinetics of catalytic incineration of (CH$_3$)$_2$S and (CH$_3$)$_2$S$_2$. They found that the Langmuir–Hinshelwood model was suitable to describe the conversion of both the VOCs. This result may be related to the sulfur-poisoning effect on the catalyst.

This study involved the catalytic incineration of dimethyl sulfide and dimethyl disulfide over MnO/Fe$_2$O$_3$ in a fixed bed reactor. The operating parameters included inlet temperature, space velocity, VOCs concentration and O$_2$ concentration. A life-test of the catalyst on both the VOCs was also performed to identify the sulfur-poisoning effect.
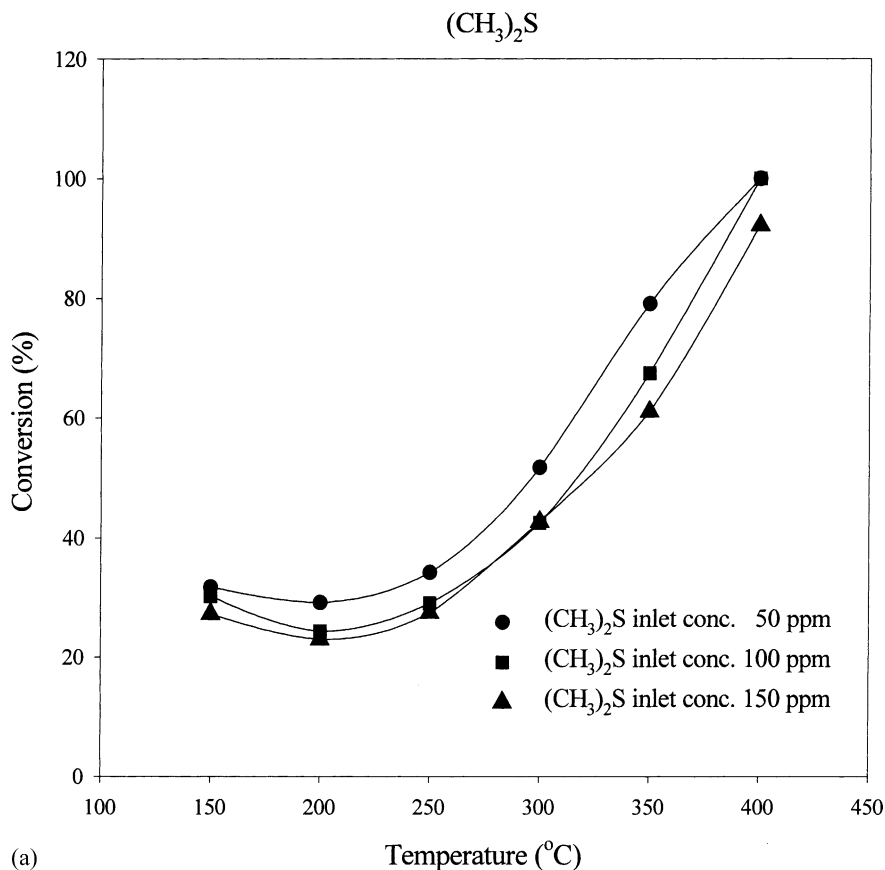

Fig. 3. (a) Affect of (CH$_3$)$_2$S concentration on the catalytic conversion of (CH$_3$)$_2$S over a MnO/Fe$_2$O$_3$ catalyst (space velocity: 55,000 h^{-1}; O$_2$ concentration: 20.8%). (b) Affect of (CH$_3$)$_2$S$_2$ concentration on the catalytic conversion of (CH$_3$)$_2$S$_2$ over a MnO/Fe$_2$O$_3$ catalyst (space velocity: 55,000 h^{-1}; O$_2$ concentration: 20.8%).
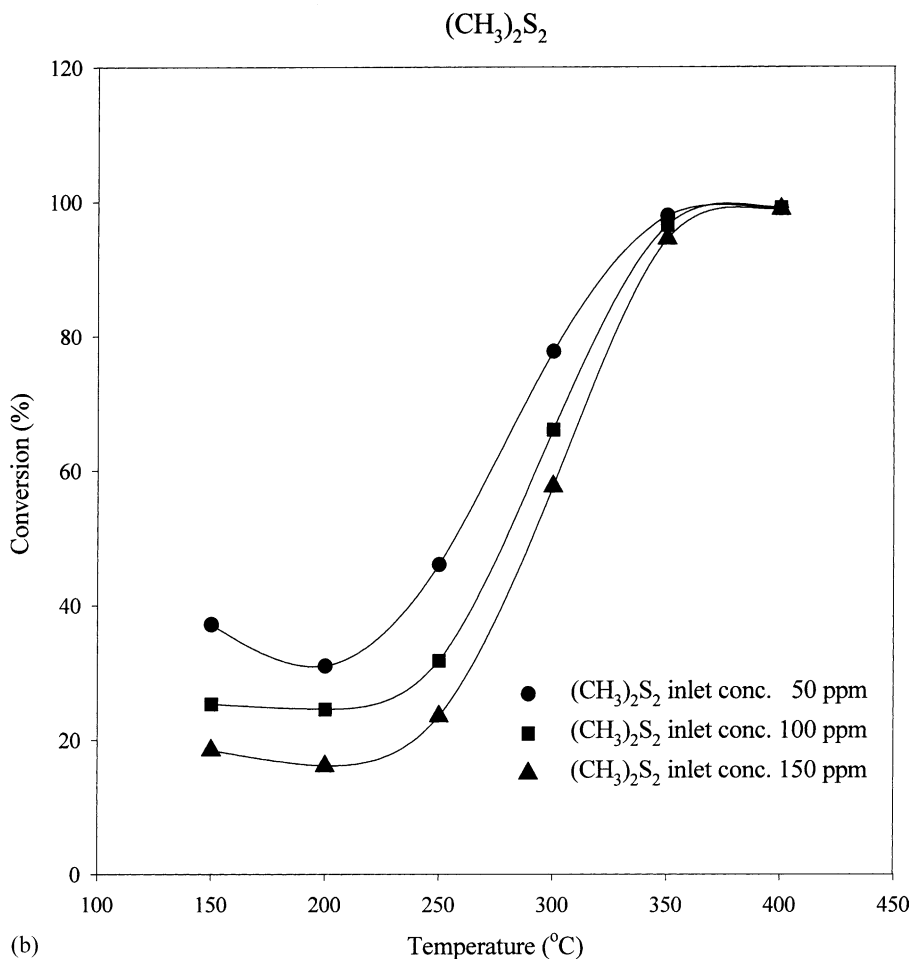
$$(CH_3)_2S_2$$

(b)

Fig. 3. (*Continued*).

2. Materials and methods

The catalytic incineration in this study was performed using a bench-scale, fixed-bed reaction system. The system can be divided into three parts: (1) an effluent gas simulation system, (2) a catalytic incineration system, and (3) a combustion gas analyzing (Fig. 1). The effluent gas simulation system was composed of an air compressor (SWAN, 1/4hp), a N_2 cylinder (99.9%, San Fu), three mass flow meters (Teledyne Hasting-Raydist, HFC-202), two plug–flow mixers (Omega, FMX7106), a water bath (Deng Yng, from −20 to 80 °C), and two VOC vapor generators (Pyrex). The flow rates of dilution N_2, purge N_2, and dilution air were controlled by three mass flow meters, to yield the desired VOC and O_2 concentrations. The feed gas was preheated before entering the reactor. The pipes, valves,

regulators, and fittings were either SS-316 or Teflon. The catalytic incineration system was composed of a custom-made 55-316 tube reactor with 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 SS316 sieve was installed in the reactor, 24 cm below the top of the tube, to support the catalyst. The catalyst packing was 7.5-mm thick. A thin layer of glass fiber and a 2-mm diameter layer of glass beads covered the catalyst packing in order to uniformly distribute the gas. Two K-type thermocouples were inserted at the top and bottom of the catalyst packing, respectively, to measure and control the inlet and outlet temperatures. The gas analysis system was composed of a GC (Shimadzu, GC-14B) and O_2 analyzer (Signal Model magneto dynamic type). The GC column was a 30 m long capillary column with a diameter of 0.53 mm (J&W Scientific #115-3432). A 1:1 splitter was connected with the column to split the sample gas into FID and FPD detectors. An ice box impingement
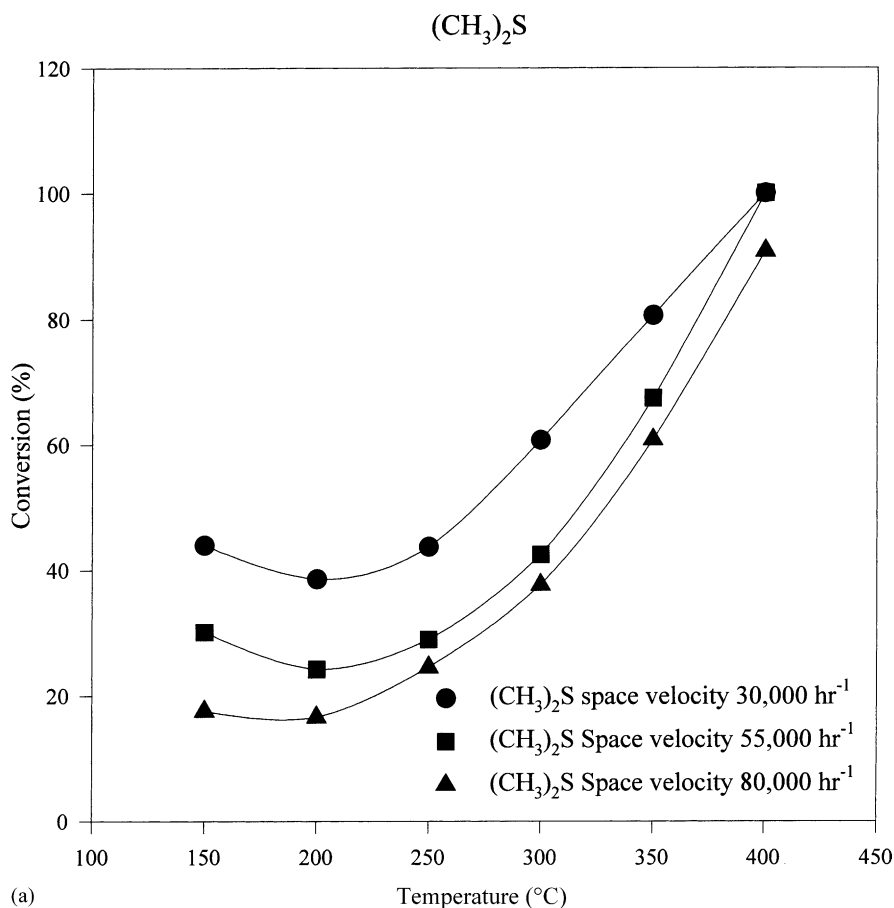
$(CH_3)_2S$

Fig. 4. (a) Affect of space velocity on the catalytic conversion of $(CH_3)_2S$ over a MnO/Fe_2O_3 catalyst ($(CH_3)_2S$ concentration: 100 ppm; O_2 concentration: 20.8%). (b) Affect of space velocity on the catalytic conversion of $(CH_3)_2S_2$ over a MnO/Fe_2O_3 catalyst ($(CH_3)_2S_2$ concentration: 100 ppm; O_2 concentration: 20.8%).
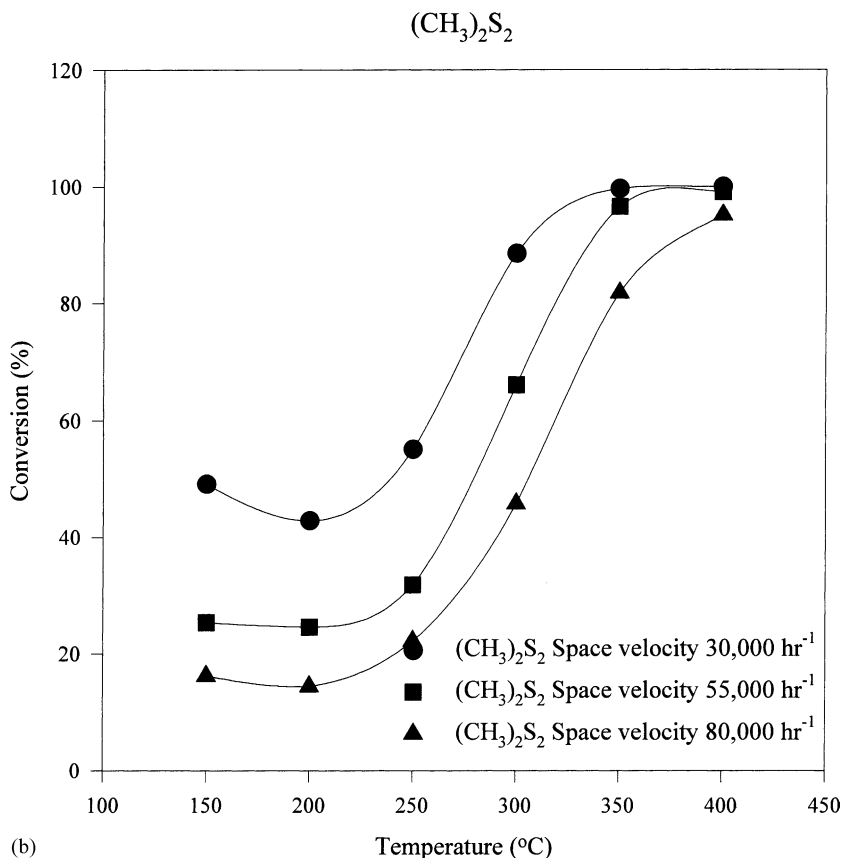
$(CH_3)_2S_2$

Fig. 4. (*Continued*).

condenser (Pyrex) and two particle filters (Balston, 95S6 and 450) were installed between the sampling port and O_2 analyzer. 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 utilizing a bubble meter (Humonic digitial flow meter 650) or a dry gas meter (Shinagawa DK-SCF-T). Standard gases included zero gas (N_2, 99.995%, San Fu), O_2 span gas (19%, San Fu), $(CH_3)_2S$ and $(CH_3)_2S_2$ span gas (200 ppm, U.S. Gas). The catalyst samples were removed before and after the reaction to determine changes in their specific surface area caused by sulfur poisoning. For this determination, a BET specific surface area analyzer (FlowSorb II 2300) was used. The catalysts used were commercial products of NISSAN GIRDLER 0-34 Cr_2O_3/Al_2O_3 and N-150 MnO/Fe_2O_3. Their properties are shown in Table 1. To determine the changes of their crystalloid, a XRD analyzer (Rigaku DIMAX III) was employed. Liquid dimethyl sulfide and dimethyl disulfide were from of Merck Chemical Inc. (purity >99%).

The experiments were divided into three series. The first series of experiments was conducted to evaluate the efficiency of two catalysts on the catalytic conversion of $(CH_3)_2S$.

The second series of experiments was performed to investigate the performance of the better catalyst, MnO/Fe_2O_3, on the catalytic conversion of both the VOCs. The operating parameters and ranges for both the VOCs were inlet temperature (150–400 °C), VOC concentration (50–150 ppm), space velocity (30,000–80,000 h^{-1}), and O_2 concentration (0.1–20.8%). The third series of experiments was a life-test of the catalyst to identify the sulfur-poisoning effects of both the VOCs.

Reagent grade liquid dimethyl sulfide and dimethyl disulfide were injected into the VOC generator, which was kept at a constant temperature of −5 °C for $(CH_3)_2S$ and 30 °C for $(CH_3)_2S_2$. Purged N_2 carried the vaporized VOCs which were mixed with dilute air and N_2 to simulate the waste gas from a typical petrochemical plant. The simulated gas was injected into the catalytic reactor in an electrically heated furnace.

Gas samples (1 ml) were taken before and after the reaction, by an on-line autosampler. These samples were injected into the GC to determine the conversion of the VOCs.
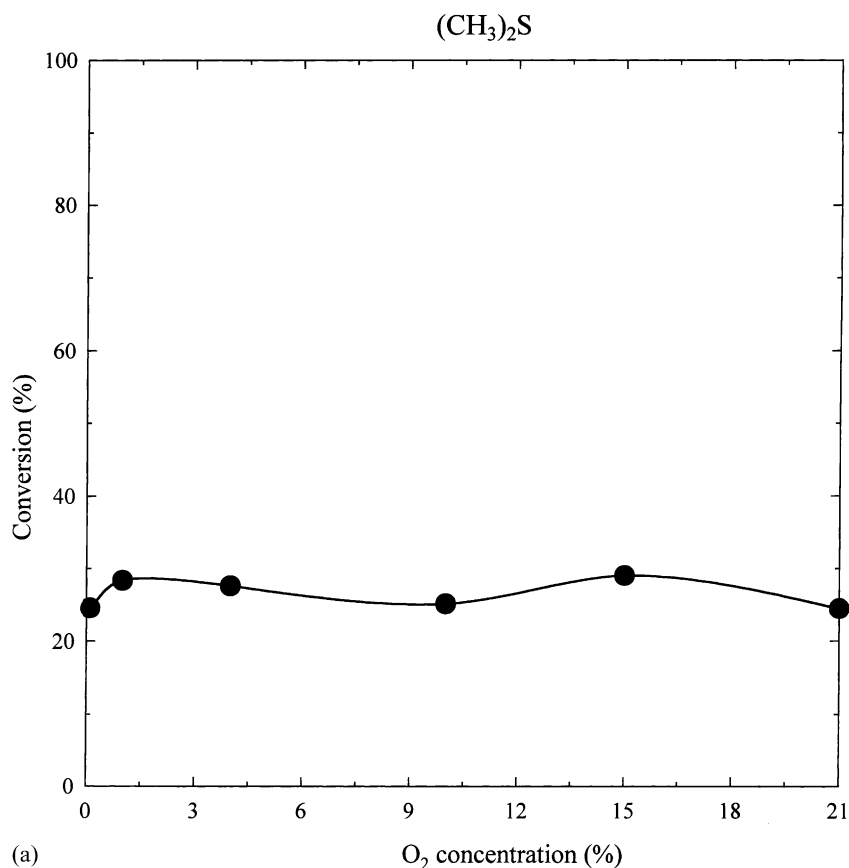

Fig. 5. (a) Affect of O_2 concentration on the catalytic conversion of $(CH_3)_2S$ over a MnO/Fe_2O_3 catalyst (inlet temperature: 250 °C; $(CH_3)_2S$ concentration: 100 ppm; space velocity: 55,000 h^{-1}). (b) Affect of O_2 concentration on the catalytic conversion of $(CH_3)_2S_2$ over a MnO/Fe_2O_3 catalyst (inlet temperatures: 250 °C; $(CH_3)_2S_2$ concentration: 100 ppm; space velocity: 55,000 h^{-1}).
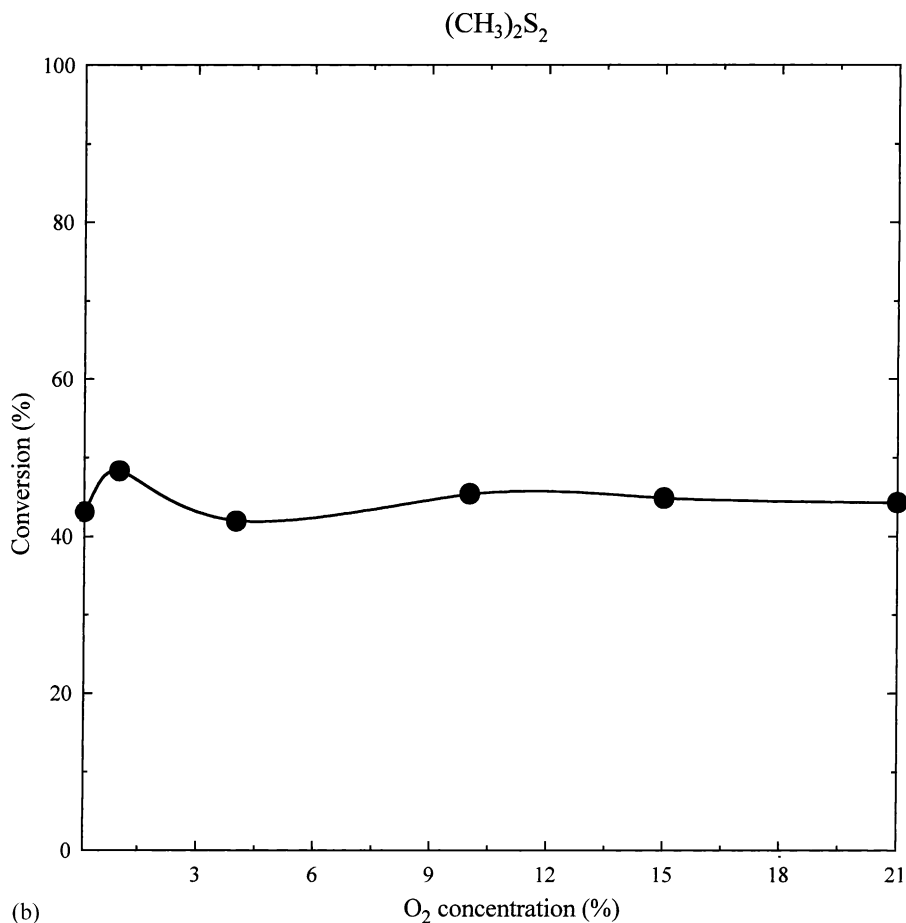
$$(CH_3)_2S_2$$

Fig. 5. (*Continued*).

A series of tests was performed earlier on the conversion of C_2H_5OH over a Pt catalyst having three size ranges [11]. The results showed that the conversion differences were not significant. Therefore, we chose the catalyst which was ground to a 50–100 mesh to carry out the experiments in this study in order to reduce both the mass transfer limitations and grinding effort.

3. Results and discussion

The conversion of sulfur-containing VOCs in a system with and without catalyst is shown in Fig. 2. In the first set of experiments, an MnO/Fe_2O_3 catalyst was used. In the second set of experiments, glass fiber was used. The tests reveal that the catalyst is the key element for the conversions of the both sulfur-containing VOCs. The preliminary tests were completed by

incinerating $(CH_3)_2S$ over the Cr_2O_3/Al_2O_3 and MnO/Fe_2O_3 catalysts. The Cr_2O_3/Al_2O_3 catalyst was as good as MnO/Fe_2O_3. However, Chu and Wu [18] showed MnO/Fe_2O_3 was a better catalyst than Cr_2O_3/Al_2O_3 for the conversion of C_2H_5SH. Therefore, MnO/Fe_2O_3 was chosen for this study.

As shown in Fig. 2, a homogeneous reaction occurs above 300 °C. This result is similar to the findings of Gonza'lez-Velasco et al. [21], in which the homogeneous reaction of methylene chloride started above 400 °C. The affect of the $(CH_3)_2S$ inlet concentration on its conversion by the MnO/Fe_2O_3 catalyst at various temperatures is shown in Fig. 3(a). This figure shows that the conversion of $(CH_3)_2S$ increases as the inlet temperature increases. Fig. 3(a) also shows that the conversion of $(CH_3)_2S$ decreases as its concentration increases from 50 to 150 ppm. This result is consistent with the results of Chu et al. [19], who used a Pt/Al_2O_3 catalyst to convert $(CH_3)_2S$ and CH3SH. Electron spectroscopy for chemical analysis (ESCA) of the fresh catalyst and the poisoned catalyst, that was used to incinerate
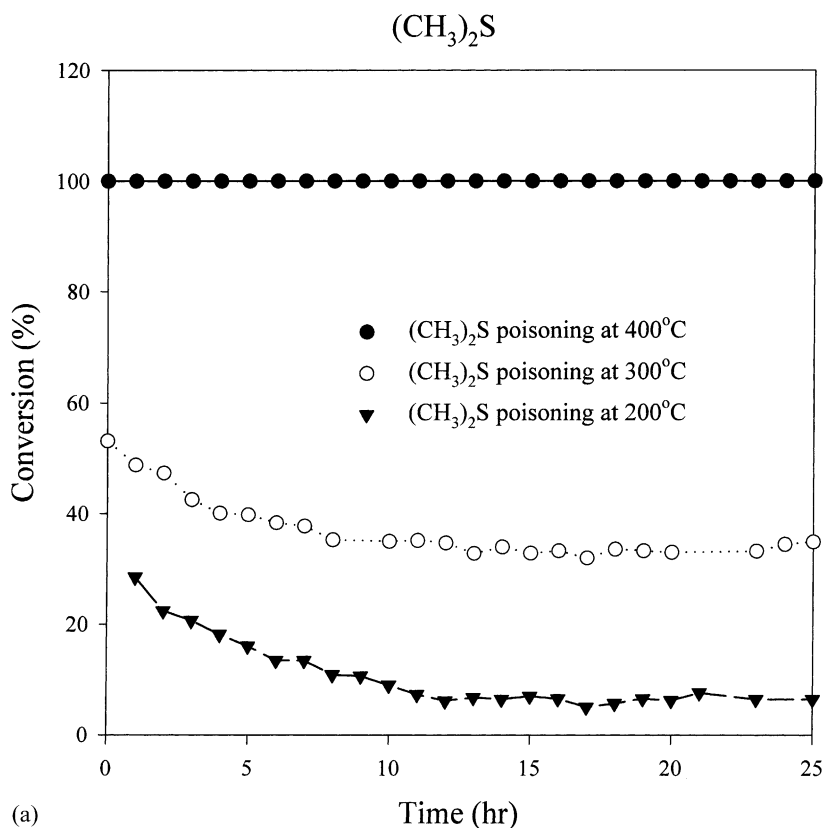

Fig. 6. (a) Poisoning effect of $(CH_3)_2S$ on the MnO/Fe_2O_3 catalyst (inlet temperatures: 400, 300 and 200 °C; $(CH_3)_2S$ concentration: 100 ppm; space velocity: 55,000 h^{-1}; O_2 concentration: 20.8%). (b) Poisoning effect of $(CH_3)_2S_2$ on the MnO/Fe_2O_3 catalyst (inlet temperatures: 350, 300 and 200 °C; $(CH_3)_2S_2$ concentration: 100 ppm; space velocity: 55,000 h^{-1}; O_2 concentration: 20.8%).

$(CH_3)_2S_2$
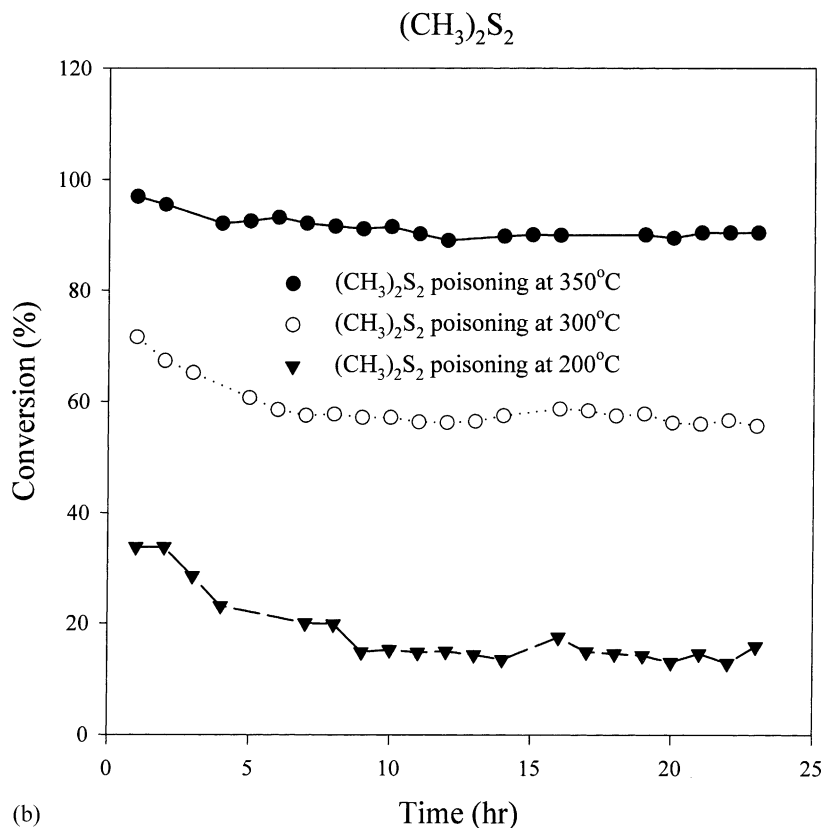
Fig. 6. (*Continued*).

150 ppm CH3SH at 315 °C, 20.8% O_2 and 50,000 h^{-1} for 32 h, was conducted in their study. Their results showed that the sulfur content on the surface of the fresh catalyst and poisoned catalyst were 0.2 and 2.8%, respectively.

These data suggest that the activated site of the catalyst in this study may also be covered by sulfur compounds especially for the high sulfur content chemical. Fig. 3(b) shows the affect of $(CH_3)_2S_2$ concentration on its conversion by the MnO/Fe_2O_3 catalyst in a temperature range of 150–400 °C. The temperature and concentration affects are similar to those for $(CH_3)_2S$.

However, a higher temperatures is required to accomplish the same $(CH_3)_2S$ conversion compared to $(CH_3)_2S_2$. Fig. 4(a) shows that the lower the space velocity, the higher the conversion of $(CH_3)_2S$. The effect of space velocity on the conversion of $(CH_3)_2S_2$ is shown in Fig. 4(b). Again, the conversion of $(CH_3)_2S_2$ decreases as the space velocity increases.

The affect of O_2 concentration on the conversion of $(CH_3)_2S$ is shown in Fig. 5(a). It was found that the affect of O_2 concentration is not significant in the range of 0.1–20.8%. This result may be related to the oxygen atoms supplied by the MnO/Fe_2O_3 catalyst itself.

Fig. 5(b) shows the affect of O_2 concentration on the conversion of $(CH_3)_2S_2$. It presents the same trend as that for $(CH_3)_2S$.

Life-tests of the MnO/Fe_2O_3 catalyst were conducted utilizing 100 ppm of $(CH_3)_2S$. In order to identify the poisoning sulfur-containing VOCs on the $MnOIFe_2O_3$ catalyst. The results are shown in Fig. 6(a).

For temperatures below $300\,°C$, the performance of the catalyst declines dramatically and then stabilizes. This phenomenon may be due to certain activated sites on the catalyst forming irreversible sulfur-poisoned sites; this process would need time to accomplish the irreversible reaction. The remaining sites of the catalyst could be reversible sulfur-poisoned sites. At $400\,°C$, however, no sulfur poisoning affect is found. This result is consistent with the results of Chu et al. [17,19,20], who showed that $(CH_3)_2S$, $(CH_3)_2S_2$ and C_2H_5SH had a poisoning effect on the Pt/Al_2O_3 catalyst and the MnO/Fe_2O_3 catalyst at lower temperatures.

Fig. 6(b) shows the sulfur-poisoning effect of $(CH_3)_2S_2$ on the MnO/Fe_2O_3 catalyst. The same trend as that for $(CH_3)_2S$ is found. Fig. 7(a) shows the specific surface areas of the MnO/Fe_2O_3 catalyst for 25-h dimethyl sulfide poisoning at varied temperatures
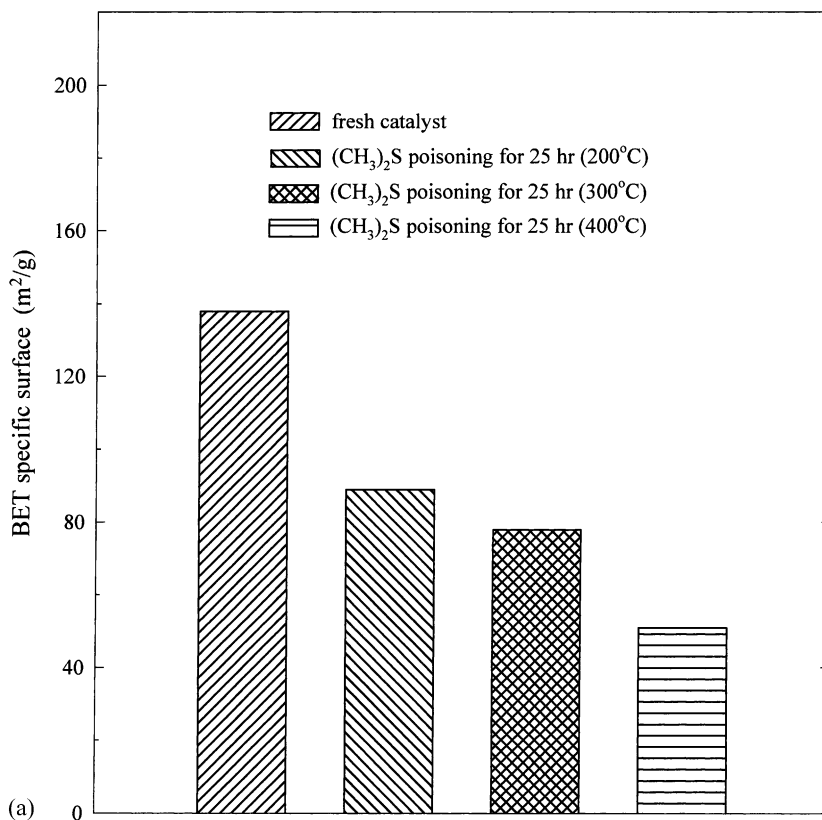

Fig. 7. (a) Specific surface area of the fresh catalyst and $(CH_3)_2S$ poisoning for 25 h at varies temperatures. (b) Specific surface area of the fresh catalyst and $(CH_3)_2S_2$ poisoning for 24 h at varies temperatures.
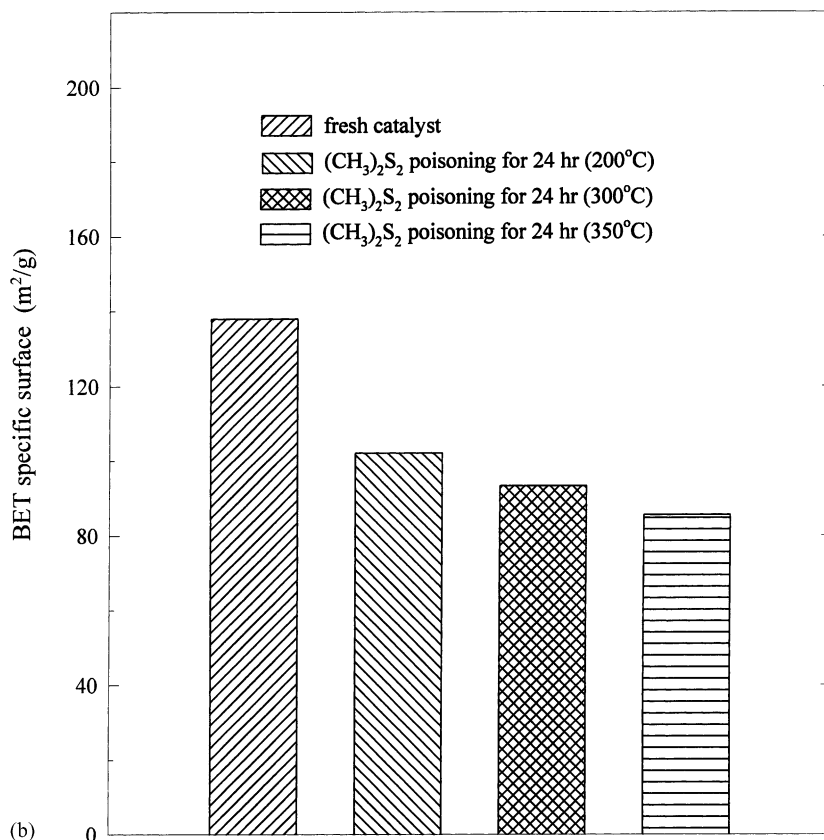
Fig. 7. (*Continued*).

(200, 300, and 400 °C) and Fig. 7(b) for 24-h dimethyl disulfide poisoning at varied temperatures (200, 300, and 350 °C). The results show that the specific surface areas of the poisoned catalysts are less than that of the fresh catalyst. This finding also suggests that the catalyst surface may be covered by sulfur compounds after the reaction. The surface area differences between the fresh catalyst and the poisoned catalyst for the case of $(CH_3)_2S$ are more dramatic than that of $(CH_3)_2S_2$.

An X-ray diffraction examination on the fresh and deactivated catalysts were conducted and the results are shown in Fig. 8. There are small peaks ($2\theta = 25.7, 27.5$ and $34.3°$) representing the ferric sulfide and manganese sulfide crystal phase appear in the spectra of the deactivated catalysts. According to the Joint Committee on Powder Diffraction System File, the small peaks represent FeS ($2\theta = 25.7°$) [760963] and MnS ($2\theta = 27.5°$ and 34.30) [882223, 401288]. As Fig. 8(a) shows the results indicated that the FeS ($2\theta = 25.7°$) and MnS peaks ($2\theta = 27.5°$) were only observed on the deactivated catalysts (300 and 400 °C). It also can be seen in Fig. 8(a) that Mn_2O_3 and Fe_2O_3 peaks due to the deactivation effect were becoming weaker and were replaced by MnS and FeS. That data in Fig. 8(a), also indicates
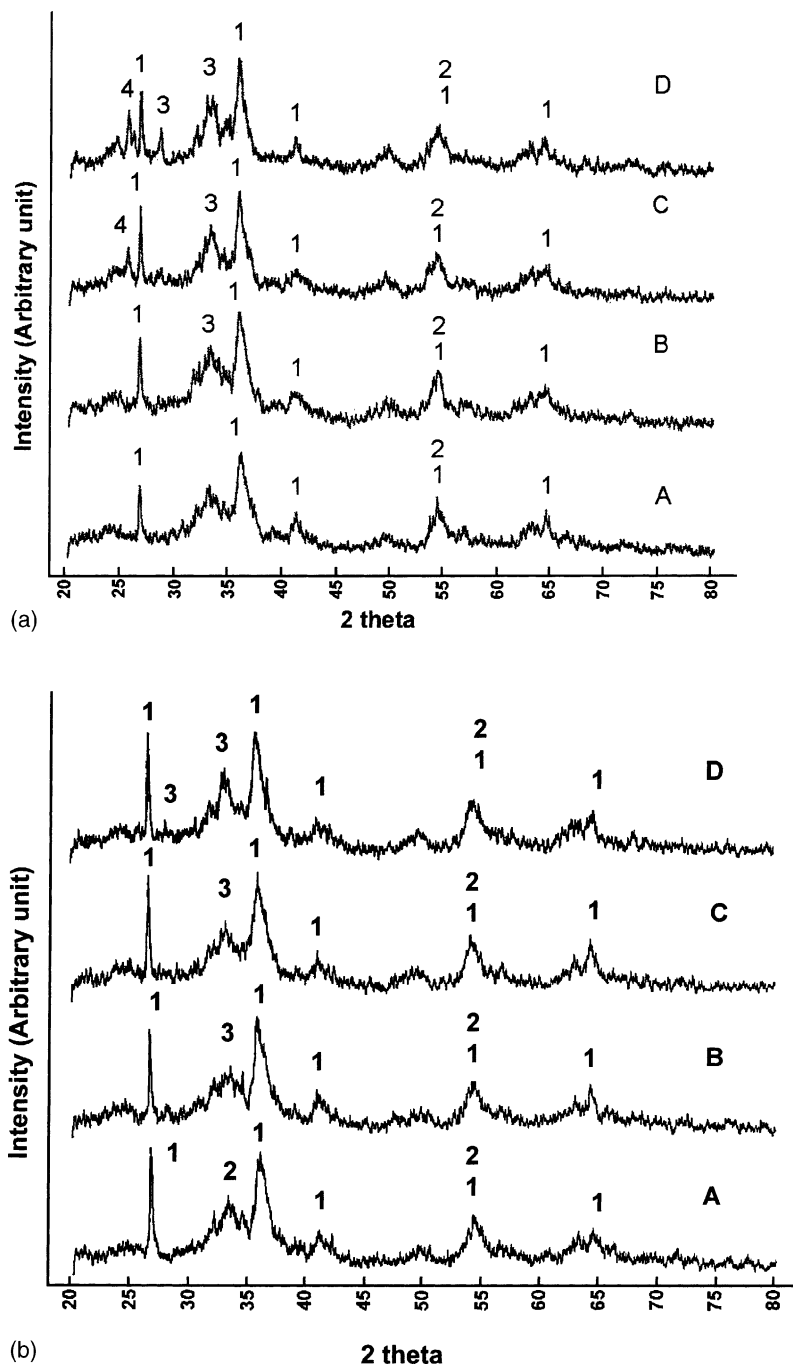
Fig. 8. (a) XRD spectra of (A) fresh catalyst and deactivated catalysts by $(CH_3)_2S$ for 25 h at: (B) 200 °C, (C) 300 °C, and (D) 400 °C (1, Fe_2O_3; 2, MnO; 3, MnS; 4, FeS). (b) XRD spectra of (A) fresh catalyst and deactivated catalysts by $(CH_3)_2S_2$ for 24 h at: (B) 200 °C, (C) 300 °C, and (D) 350 °C (1, Fe_2O_3; 2, MnO; 3, MnS; 4, FeS).

that the MnS and FeS become amorphous at low temperatures. The same phenomenon can also be found in Fig. 8(b). The results indicated that the MnS peaks ($2\theta = 27.5°$) were only observed on the deactivated catalyst (400 °C). The data in Fig. 8(b) indicated that the MnS and FeS become amorphous at low temperatures. Fig. 8(a) and (b) show that the differences of the crystalloid of the MnO/Fe_2O_3 catalyst are not significant between the fresh catalyst and the deactivated catalysts operated at various temperatures except that MnS are formed after 24–25 h and the peaks of MnS formed on the catalyst for the case of $(CH_3)_2S$ are more significant than that of $(CH_3)_2S_2$.

4. Conclusions

The catalytic incineration of $(CH_3)_2S$ and $(CH_3)_2S_2$ by Cr_2O_3/Al_2O_3 and MnO/Fe_2O_3 catalysts was conducted under a variety of operating conditions. The results show that Cr_2O_3/Al_2O_3 was not an efficient catalyst for the conversion of $(CH_3)_2S$. Consequently, MnO/Fe_2O_3 was chosen for the main experiments in this study. The results show that the conversion of VOCs increases as the inlet temperature increases and the space velocity decreases. Experiments determined that the higher the concentrations of both the VOCs, the lower were their conversions. The O_2 concentration had no effect on the conversion of both the VOCs. Both $(CH_3)_2S$ and $(CH_3)_2S_2$ had poisoning effects on the MnO/Fe_2O_3 catalyst. However, the sulfur-poisoning effects of both the VOCs were not significant once the operating temperatures exceeded 350 °C.

Acknowledgements

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