



Vapor phase oxidation of dimethyl sulfide with ozone over ion-exchanged zeolites

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ABSTRACT

This work studied the catalyst activity and stability of ion-exchanged zeolites during the oxidation of dimethyl sulfide (DMS) in the presence of ozone. Ozone was used as an oxidant to assess the oxidation capability of Ag/ZSM-5, Mn/ZSM-5 and Ag-Mn/ZSM-5 of DMS at both room temperature and 130 °C. Ion-exchange with silver ions (Ag⁺) strengthened the adsorption of DMS, resulting in an increased oxidation capacity for DMS. Furthermore, the introduction of manganese ions (Mn²⁺) strengthened the oxidation capability of DMS, thus enhancing the selectivity of SO₂ obtained from the oxidation and reducing the degradation of activity because the pores of the catalyst were blocked by the oxidation products, such as dimethyl sulfoxide (DMSO) and dimethyl sulfone (DMSO₂). Ag-Mn/ZSM-5 demonstrated a 100% conversion of DMS; not only SO₂ but also H₂SO₃ and H₂SO₄ were detected at a high GHSV (90,000 h⁻¹) and low reaction temperature (130 °C). The SO₂ adsorption curve and temperature-programmed desorption (TPD) showed that the single metal ion-exchanged zeolite had a weak adsorption capability for SO₂ at room temperature, whereas the bi-metal ion-exchanged zeolite had an excellent adsorption capability towards SO₂; it could convert SO₂ into H₂SO₃ and could convert oxidized SO₂ into H₂SO₄ in gas phase at room temperature.

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1. Introduction

Dimethyl sulfoxide (DMSO) is the main solvent in the stripping agent used by the semiconductor and display industries. DMSO has almost no odor, poses no significant harm to health and has a high solubility in water. Most of the stripping agents used are recovered by cooling absorption, and the residual stripper is channeled to a wastewater system. Under anoxic conditions in the wastewater treatment process, DMSO is reduced to dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). Both DMS and DMDS are reduced to sulfur (RS) compounds, which have been identified as major constituents of pulp and paper mill effluents. RS compounds are odorous chemicals with very low threshold concentrations and can potentially have serious impacts on environmental quality and human health [1,2].

The methods to remove RS compounds include adsorption [3,4], absorption [5], plasma destruction [6], thermal oxidation and catalytic incineration [7–13], and advanced oxidation [14]. Among these methods, thermal oxidation and catalytic incineration can treat waste gases containing high concentrations of volatile organic compounds (VOCs) and sulfur-containing volatile organic com-

pounds (SVOCs). Most catalysts employed for treating VOCs contain noble metals or base metal oxides. Usually, catalysts containing noble metals, such as Pt, Pd and Rh, are improper for treating sulfur-containing waste gases because the noble metals are easily poisoned by the sulfur compounds. Al₂O₃-supported base metal oxide catalysts have been employed with 100% conversion of 100 ppm DMS gas to SO₂ using oxygen as an oxidant under a weight hourly space velocity (WHSV) of 40,800 ml/h g at 260 °C.

The use of ozone as an oxidant offers the advantage of performing the reactions at low temperatures, which benefits the development of a cost-effective advanced oxidation technology [15]. Kastner et al. [16] used wood fly ash as a catalyst to oxidize DMS and DMDS compounds with ozone at room temperature. Their studies showed that the oxidation of DMS produced DMSO and dimethyl sulfone (DMSO₂) at low space velocities. Sahle-Demessie et al. [17–19] used V₂O₅/TiO₂, CuO/Al₂O₃ and CuO-MoO₃/Al₂O₃ as catalysts to oxidize DMS with ozone at 100–250 °C using gas hourly space velocities (GHSV) from 37,000 to 75,000 h⁻¹. Their results showed that CuO-MoO₃/Al₂O₃ has high activity and selectivity in the oxidation.

Zeolites are often used as catalytic supports and adsorbents to eliminate pollutants in the gas stream due to their unique structure and hydrophilic character. Wakita et al. [20] have used Na-Y, Na-X, Ca-X, H-β and H-ZSM-5 as adsorbents to remove DMS and *t*-butylmercaptan (TBM). They studied the phenomena when zeo-

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Table 1
The weight percents and degrees of exchange of metal ions in zeolites.

Catalysts	Metal ions (wt%)		Exchange ratio (%)	
	Ag	Mn	Ag	Mn
Ag/ZSM-5	1.54	0.01	45.8	0.6
Mn/ZSM-5	0.02	0.84	0.6	48.3
Ag-Mn/ZSM-5	1.46	0.99	43.4	56.8
			Under-exchanged	Under-exchanged

lites of different structures adsorbed DMS and TBM. However, both the initial removal efficiency and saturation adsorption capacities of DMS on the adsorbents mentioned were too low to be used in the filtration system of a clean room. Satokawa et al. [21] used Ag/Na-Y to adsorb DMS and found that the capacities of the adsorbents increased with the silver content in the adsorbents.

In this work, we studied the removal efficiency of DMS of catalysts under conditions with or without ozone at room temperature, and we investigated the conversion of DMS and the selectivity for SO₂ with ozone over ion-exchanged zeolites at relatively low temperatures. Temperature-programmed desorptions (TPDs) of the products on zeolites after oxidation were also determined. This study reports the effects of various reaction variables, such as temperature and GHSV, on the catalytic activity and stability during the oxidation of DMS. Furthermore, this work also measured the SO₂ adsorbing performance and TPDs to ensure that the bi-metal ion-exchanged zeolites did not only convert DMS to SO₂ but also further convert SO₂ to H₂SO₃ and oxidize SO₂ to H₂SO₄.

2. Experimental

2.1. Preparation of adsorbents

NH₄⁺-ZSM-5 (CBV-5524G, SiO₂/Al₂O₃ = 50, surface area = 425 m²/g), as-purchased from Zeolyst Corp., was used for preparing Ag/ZSM-5 and Mn/ZSM-5 through the conventional ion-exchange procedure by reacting NH₄⁺-ZSM-5 with aqueous solutions of AgNO₃ and Mn(CH₃COO)₂, respectively, at 50 °C. Ag-Mn/ZSM-5 was prepared according to the following procedure. First, the as-received zeolite (20 g) was mixed with water (120 ml at 50 °C) under vigorous stirring, and 15 ml of 0.55 M AgNO₃ aqueous solution was added dropwise into the suspension and this mixture was stirred for 2 h at 50 °C. After filtration and washing with deionized water, the cake-like mixture was re-dispersed in deionized water at 50 °C, and 20 ml of 0.47 M Mn(CH₃COO)₂ aqueous solution was added dropwise; this mixture was then stirred for 2 h. The color of the solution changed from white to pale gray after stirring. After filtration and rinsing with deionized water, the mixture was dried at 80 °C, followed by calcination at 420 °C for 3 h. After pelletizing, crushing and sieving (16–30 mesh), the as-prepared adsorbents were ready for use. The weight percents of Ag in Ag/ZSM-5, Mn/ZSM-5 and Ag-Mn/ZSM-5 were 1.54%, 0.02% and 1.46%, respectively, and the weight percents of Mn were 0.01%, 0.84% and 0.99%, respectively. The weight percents and degrees of exchange of metal ions in the zeolites are presented in Table 1.

2.2. Adsorption and catalytic activity measurements

Measurements of adsorption and catalytic activity were made in a fixed-bed double-layer glass reactor (11.5 mm inner diameter). The volume of adsorbent was 1 cm³ (0.36–0.47 g), and the temperature was adjusted using a cycling oil bath. DMS/air and SO₂/air with specific concentrations were prepared by diluting 2038 ppm DMS/N₂ and 998 ppm SO₂/air gas with air, respectively. The humidity ratio of the inlet gas was about 10 g/kg dry air. The ozone was

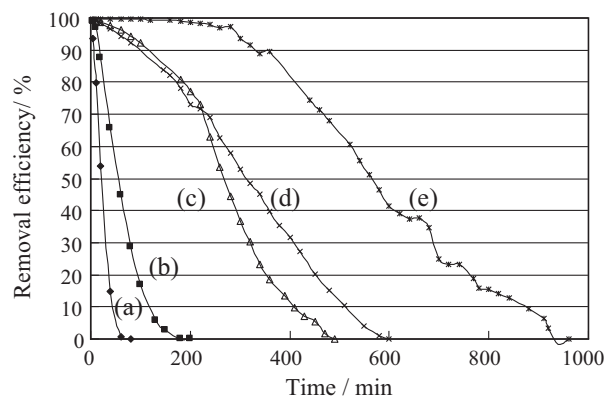


Fig. 1. Adsorption curves of DMS/air without and with ozone on (a) NH₄⁺-ZSM-5, (b) Ag/ZSM-5, (c) NH₄⁺-ZSM-5 + O₃, (d) Ag/ZSM-5 + O₃, at GHSV = 180,000 h⁻¹ and room temperature and (e) Ag/ZSM-5 + O₃ at GHSV = 90,000 h⁻¹ and room temperature.

generated by commercial equipment (High quality ozonizer, Model TR-300, TAIREX Corporation, Ltd.), and the concentrations of ozone in the inlet and outlet gases were detected with an ozone analyzer (Ozone analyzer, Model UV-100, ECO SENSORS, INC.). The flow rates of SO₂/air, DMS/N₂, air and ozone were adjusted using mass flow controllers. The GHSV was varied from 45,000 to 180,000 h⁻¹, and the corresponding residence time in the reactor was varied between 0.08 and 0.02 s. The concentrations of DMS in the inlet and the outlet gases as well as the concentration of SO₂ in the outlet gas were analyzed with a pulsed fluorescence H₂S-SO₂ analyzer (Model 450C, Thermo Electron Corporation.) at a resolution of 1 ppb.

2.3. Characterization of adsorbent

TPD was carried out with an automatic temperature-programmed desorption apparatus equipped with a quadrupole mass detector (Thermo VG ProLab). Samples (0.2 g) were placed in a U-type quartz tube. The TPD program began with a He (30 ml/min) flush at 50 °C for 60 min; the temperature was then increased to 900 °C at a rate of 10 °C/min. The ionic intensities of mass-to-charge ratio (*m/e*) in the desorbed gas: 62, 64, 78, and 94, were analyzed by the mass spectrometer. The cooling liquid product of DMS oxidation reaction was analyzed by ion chromatography (Dionex ICS-90, column AS14 4 mm) using 1.0 mM NaHCO₃/3.5 mM Na₂CO₃ as eluent.

3. Results and discussion

3.1. Removal efficiency of NH₄⁺-ZSM-5 and Ag/ZSM-5

Fig. 1 shows the variations in removal efficiency of NH₄⁺-ZSM-5 and Ag/ZSM-5 for 20 ppm DMS with or without ozone. As shown in Fig. 1, the removal efficiency of zeolites for DMS was poor without ozone, regardless of whether there was ion-exchange or not. Nevertheless, the adsorption time of DMS on Ag/ZSM-5 was longer than that of unmodified NH₄⁺-ZSM-5, showing that Ag⁺ in zeolites can assist in the adsorption of DMS.

The DMSO and DMSO₂ produced from the oxidation of DMS by ozone [16] can be easily adsorbed by zeolite or adhere onto the zeolite surface because the boiling temperature of DMSO is 189 °C and DMSO₂ is solid at ambient temperatures. Under conditions with a ratio of O₃/DMS = 1/1, the initial removal efficiency of Ag/ZSM-5 was close to unmodified NH₄⁺-ZSM-5, but its removal capability for DMS was significantly increased, and the adsorption time was still longer than that of NH₄⁺-ZSM-5.

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