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Sulfur resistance and high activity of hydrated manganese sulfate in the catalytic oxidation of methanethiol ☆

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Abstract

Hydration of manganese sulfate at a low reaction temperature (150 °C) induces high heterogeneous catalytic activity and stability in the oxidation of methanethiol. The temperature of the reaction controls the reversible change of structure, i.e., hydration/dehydration processes as well as the associated changes of activity and selectivity.

Keywords: Metal sulfate catalyst; Oxidation; Hydration; Sulfur resistance

1. Introduction

Sulfur is a well-known source of poisoning of heterogeneous catalysts. When oxidation reactions are performed in the presence of sulfur compounds, the formation of metal sulfates is usually evidenced as the main deactivation cause of transition-metal oxides [1]. Transition-metal oxide catalysts are nonetheless highly active toward total oxidation reactions [2]. For example, Lahousse et al. [3] have shown that γ-MnO_2 is a very promising catalyst which is more active for total oxidation reactions than conventional catalysts based on noble metals. Owing to their low toxicity and low cost, manganese oxides are now widely used in commercial systems and are studied by many research groups [3–8]. However, these catalysts are very sensitive to the presence of sulfur, leading to the formation of manganese sulfate [8–11]. Heyes et al. [9] have nonetheless reported that a sulfated MnO_2 catalyst remains moderately active in the oxidation of volatile organic compounds. They also tested the activity of a $MnSO_4$ sample and showed that it was active in the removal of methanethiol [12]. Wang and Weng [13] have also reported that the impregnation of sulfates on CuO/Al_2O_3 catalysts improves their activity in the destructive oxidation of dimethyl disulfide. The catalytic activity of transition-metal sulfates in acid–base reactions is well known. Furthermore, Tanabe and Takeshita [14] reported that the acidity and acid–base activity of various transition-metal sulfates including manganese sulfate depend on their content of hydration water. In this paper, we report the unexpected activity and behavior of $MnSO_4{\cdot}H_2O$ in the oxidation of methanethiol and compared it to the activity of a conventional manganese oxide catalyst.

2. Experimental

2.1. Catalysts

Manganese sulfate monohydrate ($MnSO_4{\cdot}H_2O$) was purchased from Merck (Ref. 1.059999.1000) and γ-MnO_2 was provided by Erachem Europe S.A. (Tertre, Belgium).

2.2. X-ray diffraction

X-ray diffraction of the samples was carried out in a Kristalloflex Siemens D-5000 powder diffractometer with $\mathrm{Cu}K_{\alpha 1,2}$ radiation ($\lambda = 1.5418$ Å). The 2θ range between 2 and 85° was scanned at a rate of $0.02^\circ\ \mathrm{s}^{-1}$. The sample powders were mounted on silicium monocrystal sample holders. Identification of the phases was carried out using the JCPDS database [15].

☆ This paper is dedicated in memory of Professor Paul Grange.

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2.3. *Catalytic tests*

Catalytic tests were carried out at atmospheric pressure in a fixed-bed flow microreactor. The reaction feed was a 100 ml min^{-1} flow of a mixture of 250 vppm methanethiol (Indugas, 5000 vppm in N_2) and 20 vol% O_2 (Indugas, 99.995%) in N_2 (Indugas, 99.995%). Some tests were also performed in the presence of water vapor at a concentration of approx 20,000 vppm. The catalytic tests were performed with a sample of 0.112 g of $MnSO_4{\cdot}H_2O$ (corresponding to 0.1 g of anhydrous $MnSO_4$) or 0.1 g of γ-MnO_2 sieved between 0.2 and 0.315 mm. The catalyst was diluted in 7 cm^3 of glass beads of the same diameter (previously checked to be inactive). The reactant and the products of the incomplete oxidation were analyzed by on-line gas chromatography (Varian CP-3800 gas chromatograph with a capillary column WCOT fused silica, 15 m × 0.32 mm i.d., coating CP-SIL 5 CB) and quantified using a flame ionization detector (FID). The gaseous outlet was also analyzed by an on-line mass spectrometer (Balzers Thermostar GSD300 T2 gas analyzer system equipped with a quadrupole mass spectrometer QMS200). The catalysts were heated in situ at the reaction temperature under a pure oxygen flow (50 ml min^{-1}). Before measurement of the conversion, the temperature was maintained for 30 min. The time on stream is defined as the time from which the reactant feed is introduced in the reactor. The results are expressed in term of methanethiol (MSH) conversion calculated on the basis of its disappearance from the reactant flow.

3. Results and discussion

The conversion of methanethiol was first measured over $MnSO_4{\cdot}H_2O$ and γ-MnO_2 as a function of time at 150 °C. Fig. 1 shows that on the one hand γ-MnO_2, as expected, loses its activity with time on stream. Characterization of γ-MnO_2 after 15 h of reaction at 150 °C by XPS shows a very low reduction of its surface and deposition of sulfate species at the catalyst surface. However, no bulk manganese sulfate, reduction, or phase transformation was detected by XRD. The accumulation of sulfate species at the surface of γ-MnO_2 is assumed to explain the decrease of activity observed over this sample. On the other hand, the activity of $MnSO_4{\cdot}H_2O$, which was almost inactive at the beginning of the reaction, progressively increased with the time on stream to reach 100% of conversion (Fig. 1). A kind of "activation" period thus seems required to initiate the catalytic activity of the $MnSO_4{\cdot}H_2O$ sample. Methanol was identified as the main organic product formed during the reaction at 150 °C over both catalysts. Tentative identifications of the inorganic products (CO, CO_2, H_2O, H_2S, SO_2, or SO_3) which can be formed during the reaction were also carried out using an on-line mass spectrometer equipment. However, the high number of the different potential species present in the outlet flow, the common ionization fragments for these species, and the high baseline level recorded for some ions made it impossible to evidence CO, CO_2, H_2O, or H_2S formation. Only the evolution of some higher masses (47, 64, and 80) could be used. The profile of the mass (47) corresponding to methanethiol followed the methanethiol conversion calculated on the basis of the chromatographic data. Moreover, sulfur oxides were detected when a conversion of the methanethiol was observed over the $MnSO_4{\cdot}H_2O$ sample. Since the ionization of SO_3 in the mass spectrometer gives the same ionization fragments as SO_2, it is not possible to distinguish if only SO_3 is formed or both SO_2 and SO_3 are formed. The formation of sulfur oxides progressively increased with time on stream and the decrease of the methanethiol intensity. This shows that an oxidation of sulfur is occurring during the conversion of the methanethiol at 150 °C over the $MnSO_4{\cdot}H_2O$ sample. Concerning H_2S, one cannot draw any conclusion because the mass (34) at which it should be observed is identical to that of the isotopic fraction of oxygen ($O^{16}O^{18}$). However, one can reasonably assume that, under the sulfur-oxidizing conditions induced by the catalyst (formation of SO_x), H_2S would be oxidized as efficiently as methanethiol.

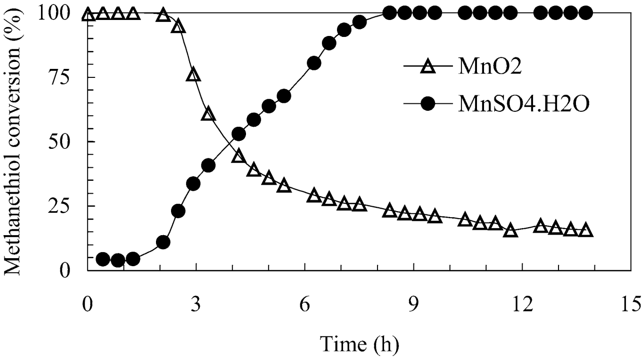

Fig. 1. Variation in the conversion of methanethiol at 150 °C with time on stream using $MnSO_4{\cdot}H_2O$ and γ-MnO_2 as catalysts.

The conversion was then measured over both samples as a function of temperature between 100 and 280 °C. First, the temperature was maintained for 15 h at 150 °C and then decreased from 150 to 100 °C. The temperature was maintained for 1 h at 100 °C and then increased from 100 to 280 °C in steps of 20 °C. At each temperature step, the temperature was maintained for 1 h in order to perform several GC analyses of the gaseous outlet. Fig. 2 shows the average methanethiol conversion measured over $MnSO_4{\cdot}H_2O$ and γ-MnO_2 as a function of the increasing temperatures. As shown in Fig. 2, $MnSO_4{\cdot}H_2O$ again appeared more active than γ-MnO_2 since the conversion of methanethiol reached 100% at 150 °C over the sulfate catalyst.

In order to determine if the period of "activation" observed at 150 °C over the $MnSO_4{\cdot}H_2O$ sample can be decreased, the conversion of methanethiol was investigated as a function of time at higher temperatures, namely 220 and 280 °C. Before the sample was in contact with the reaction mixture, $MnSO_4{\cdot}H_2O$ was heated in the reactor to

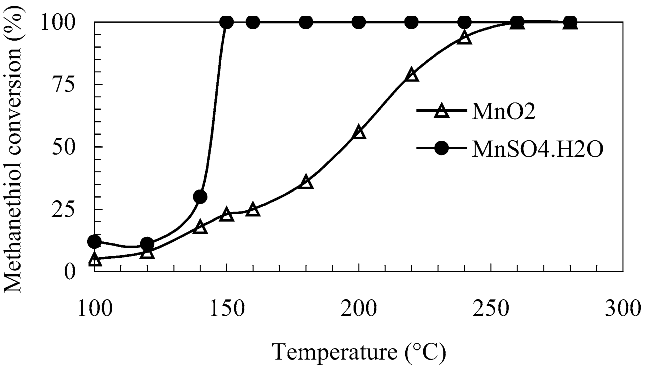

Fig. 2. Variation in the conversion of methanethiol with reaction temperature using $MnSO_4 \cdot H_2O$ and γ-MnO_2 as catalysts.

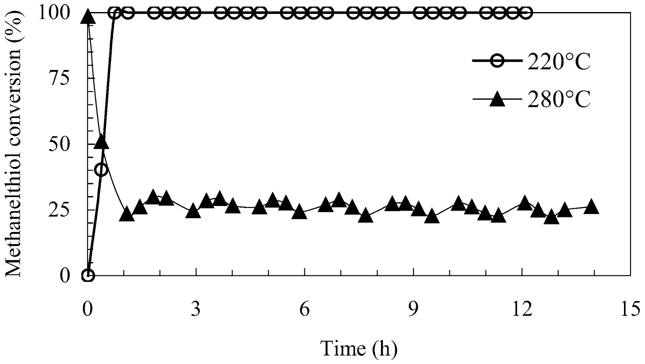

Fig. 3. Conversion of 250 vppm methanethiol as a function of time on stream at 220 and 280 °C using $MnSO_4 \cdot H_2O$ as catalyst.

Table 1
Conversion of methanethiol and yields of methanol and dimethyl disulfide measured after 15 h of reaction over $MnSO_4 \cdot H_2O$

Temperature	150 °C	220 °C	280 °C
Methanethiol conversion	100	100	27
Methanol yield	32	57	2
Dimethyl disulfide yield	0	0	8

the reaction temperature under a pure oxygen flow. Fig. 3 shows the conversion of methanethiol measured as a function of the reaction time at 220 and 280 °C. The conversion of methanethiol rapidly reached 100% at 220 °C while it quickly decreased from 100 to 25% at 280 °C. At 220 °C, methanol was again detected in the outlet flow as the main organic product of the oxidation of methanethiol (see Table 1). In contrast, the formation of methanol was strongly reduced at 280 °C and dimethyl disulfide (DMDS) was identified as the main organic by-product of the reaction. The conversion of methanethiol and yields of methanol and dimethyl disulfide measured after 15 h of reaction are summarized in Table 1.

In order to explain the difference of activity observed between 150 and 280 °C, X-ray diffraction analyses of the $MnSO_4 \cdot H_2O$ samples after the test reaction were recorded. No enlargement or shift of the X-ray diffraction lines was detected after reaction at 150 °C. The XRD lines recorded on the fresh sample and after reaction at 150 °C could be attributed to the $MnSO_4 \cdot H_2O$ phase (JCPDS standard file No 33-0906) [15]. After reaction at 280 °C, important modifications of the diffraction pattern were observed. Comparison of the diffraction lines with standard JCPDS patterns [15] indicates that the new main XRD lines can be assigned to the anhydrous $MnSO_4$ phase next to some much smaller lines assigned to the hydrated sulfate. It has been reported that anhydrous $MnSO_4$ is very hygroscopic and hydrates in ambient air [16]. Therefore, the coexistence of $MnSO_4 \cdot H_2O$ and $MnSO_4$ after reaction and calcination at 280 °C is postulated to be due to a hydration of the surface layers of the anhydrous manganese sulfate during handling.

The following explanation of the performance of the $MnSO_4 \cdot H_2O$ sample may be given. It is assumed that anhydrous and hydrated $MnSO_4$ phases exhibit very different activities. Around 280 °C, the $MnSO_4 \cdot H_2O$ phase completely dehydrates and loses its activity. A thermogravimetric analysis of the dehydration of $MnSO_4 \cdot H_2O$ was performed by Lendormy [17]. Her work shows that the loss of crystallization water occurs between 150 and 270 °C and

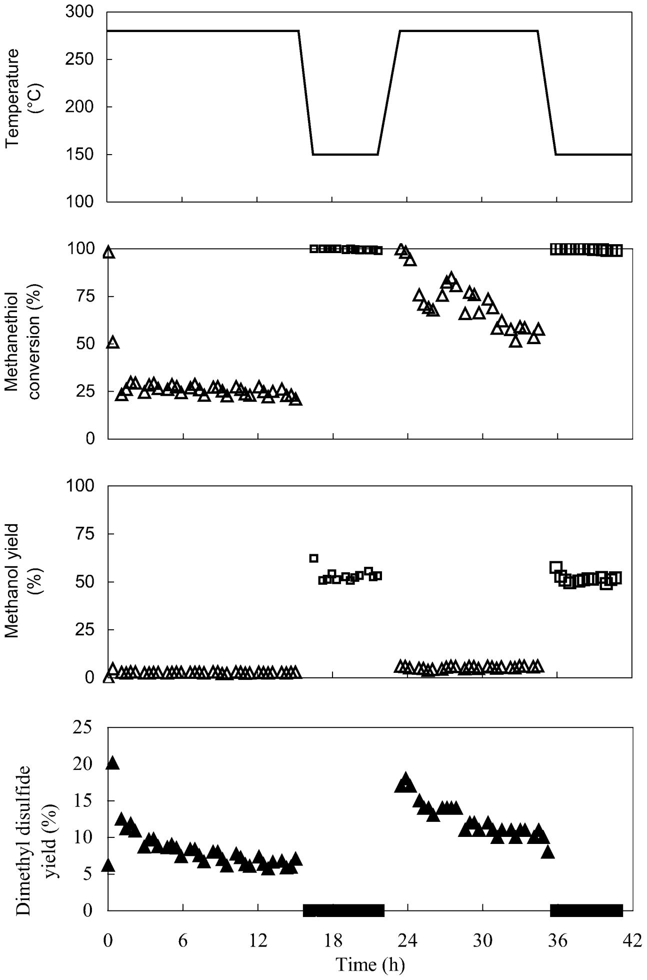

Fig. 4. Conversion of 250 vppm methanethiol and yields of methanol and dimethyl disulfide as a function of time on stream and reaction temperature using $MnSO_4 \cdot H_2O$ as catalyst.

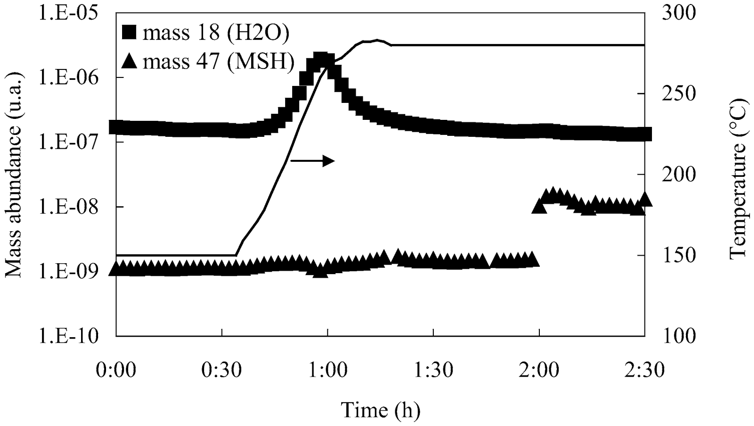

Fig. 5. Evolution of the masses 18 and 47 as a function of time when increasing the reaction temperature from 150 to 280 °C using $MnSO_4 \cdot H_2O$ as catalyst.

that the anhydrous $MnSO_4$ phase is formed over 270 °C. Tanabe and Takeshita [14] reported that the number of acid sites present on various metal sulfates increases as the dehydration proceeds but that the sites disappear completely in the anhydrous form.

The presence of hydration water in manganese sulfate is thus assumed to control its activity. A test was performed with a fresh $MnSO_4 \cdot H_2O$ sample whose the activity was first measured at 280 °C for 15 h, and then the temperature was decreased and increased between 280 and 150 °C. Fig. 4 shows that activations/deactivations of the sulfate catalyst were observed at 150 and 280 °C, respectively. Moreover, a high water desorption was observed by mass spectrometry during the heating at ~10 °C/min of the sample from 150 to 280 °C under the reactant flow. Fig. 5 shows that this water desorption began around 170 °C and reached its maximum at about 260 °C. In contrast, since water is produced by the oxidation of methanethiol, a rehydration of anhydrous manganese sulfate must occur at 150 °C and improve its activity when the temperature is decreased from 280 to 150 °C. The hydration and activation of $MnSO_4$ therefore appears to be a reversible phenomenon that controls the catalytic activity. Moreover, changes in the yields of dimethyl disulfide and methanol with temperature were also observed. At 150 °C, the hydrated phase appears to favor the formation of methanol while dimethyl disulfide is formed on the anhydrous phase. The formation of methanol from methanethiol necessitates the scission of the C–S bond in CH_3SH, whereas the formation of dimethyl disulfide requires the scission of the S–H bond. Different reaction pathways and active sites are thus assumed as a function of the temperature and subsequent hydration of the manganese sulfate phase.

In order to check the role of oxygen and water in the reaction, some tests were performed at 150 °C in the presence of water vapor (approx 20,000 vppm) in the feed and in absence of oxygen. These tests showed that $MnSO_4 \cdot H_2O$ becomes inactive in the absence of oxygen in the feed, regardless if water vapor (approx 20,000 vppm) is added in the inlet flow. However, the presence of water in the feed increased the methanol yield. On the one hand, our results show that the methanethiol stops being converted immediately after the oxygen feed was shut off. On the other hand, the methanethiol started to be converted again as soon as oxygen is reintroduced in the feed. These results demonstrate that an oxidation mechanism is occurring over the manganese sulfate catalyst. Since the presence of oxygen is required to convert methanethiol and produce methanol, the following reaction $CH_3SH + H_2O \rightarrow CH_3OH + H_2S$ cannot explain the formation of methanol.

A test was also performed in the presence of water vapor (approx 20,000 vppm) at 280 °C. This test showed that the high activity of the manganese sulfate (i.e., 100% conversion of methanethiol) can be maintained at this temperature in the presence of a high concentration of water in the feed. Besides modifying the activity, the presence of a large amount of water vapor in the flow at 280 °C also prevents the formation of dimethyl disulfide and favors the formation of methanol. These results confirm that the hydration of the manganese sulfate controls both its activity and its selectivity.

4. Conclusions

This work shows that manganese sulfate is more active and sulfur resistant in the catalytic oxidation of methanethiol than a conventional manganese oxide catalyst. The high oxidation activity of the manganese sulfate is nonetheless strongly controlled by the presence of hydration water. The hydration/dehydration of manganese sulfate and subsequent activation/deactivation are reversible phenomena.

Acknowledgments

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