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Zeolite and Metal Oxide Catalysts for the Production of Dimethyl Sulfide and Methanethiol

Craig P. Plaisance · Kerry M. Dooley

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Abstract Metal oxide and zeolite catalysts were examined for the production of methanethiol and dimethyl sulfide by condensation of methanol and hydrogen sulfide. Catalyst acid sites were characterized by investigating the desorption of 1-propanamine. Catalysts as diverse as WO_3/ZrO_2, La_2O_3/Al_2O_3, γ-Al_2O_3, and H-MFI were active and selective in the production of dimethyl sulfide.

Keywords Dimethyl sulfide · Methanethiol · Methanol condensation · Acid strength distribution

1 Introduction

Dimethyl sulfide (DMS) and methanethiol (MT) are produced by the condensation of hydrogen sulfide with methanol (MeOH) over a metal oxide or zeolite catalyst. The general reactions are $H_2S + MeOH \rightarrow MT + H_2O$ and $H_2S + 2MeOH \rightarrow DMS + 2H_2O$. In addition to forming sulfur products (DMS and MT), methanol condenses to dimethyl ether (DME), which can dehydrate to ethylene. The DMS and MT can also react further with H_2S to produce higher molecular weight sulfides.

Methanethiol is used to produce methionine which is used as feed additive and in pharmaceutical production. Dimethyl sulfide is used to produce dimethyl sulfoxide which is used as a solvent and in pharmaceutical production [1].

The primary molecules involved in the condensation reactions are MeOH, DME, MT, DMS, H_2S, and H_2O, all of which can be activated by associative adsorption onto Lewis acid centers, protic (Bronsted) centers, and basic centers on the catalyst surface [2, 3]. Further activation can occur by dissociative adsorption (especially for MeOH, MT, H_2S) on pairs of Lewis acid and base sites [3–6].

Several mechanisms have been proposed for the reactions between methanol and H_2S on metal oxide and zeolite surfaces. Mashkina et al. [2] proposed a serial mechanism by which surface methoxy and bisulfide species on Lewis centers interact to form MT, which then desorbs. MT also adsorbs on Lewis centers, reacting with a methoxy group to form DMS. According to Mashkin et al. [1], the disproportionation of two molecules of MT to DMS and H_2S occurs on strong acid sites such as a pair of Lewis centers, and DME is formed when surface methoxy species interact with each other or with gas phase methanol. Other mechanisms suggest that DMS is formed by the reaction of surface methoxy species with gas phase H_2S [7, 8], or the reaction of gas phase H_2S and DME [9]. The overall reactions suggested by these mechanisms are:

$$MeOH + H_2S \rightarrow MT + H_2O \quad (1)$$

$$MeOH + MT \rightarrow DMS + H_2O \quad (2)$$

$$2MeOH \rightarrow DME + H_2O \quad (3)$$

$$2MT \rightarrow DMS + H_2S. \quad (4)$$

Mashkina et al. [2] studied silica, silica-alumina, and alumina supports doped with transition metal oxides. They found that alumina-supported catalysts were an order of magnitude more active than silica-alumina-supported catalysts, which were themselves an order of magnitude more active than silica-supported catalysts. A conclusion from their results is that catalysts with Lewis centers of modest acid strength, such as alumina, are the most active

C. P. Plaisance · K. M. Dooley (✉)
Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA
e-mail: dooley@lsu.edu

for this reaction, while catalysts with either strong (silica-alumina) or weak (silica) Lewis centers are less active; note that pure silica cannot easily dissociate either methanol or H_2S [3, 10]. Additionally, the more basic metal oxides tend to be more selective for MT, while the more acidic metal oxides are more selective for DMS [1, 2, 11].

Several X and Y zeolites containing different cations from the alkali series have been characterized for these reactions [9]. The protonated forms of these zeolites were found to be much more active for reaction to MT and DMS than deprotonated forms [7–9]. Other studies found that HZSM-5 was the most active of the common zeolites for this reaction [7, 8]. Additionally, it was concluded that reaction (4) is faster on zeolites than either (1) or (2).

The aim of this work is to identify zeolite and metal oxide catalysts suitable for the production of either DMS or MT in high selectivity at high methanol conversion, and also to determine optimal reaction conditions for these selective catalysts. Properties used to gauge the suitability of catalysts included activity, selectivity toward the desired products, rate of deactivation, ease of regeneration of the catalyst, and whether or not the side products could be recycled. Key reaction conditions were optimized for each catalyst: temperature, space velocity, and feed ratio of methanol to hydrogen sulfide. Finally, a simple mechanism is proposed to explain trends in the effects of catalyst acid strength on activity and selectivity as found both in the literature and in this work.

2 Experimental

In this work ten different metal oxide and zeolite catalysts were used, as shown in Table 1. La_2O_3/Al_2O_3, Al_2O_3, and TiO_2/SiO_2 were acquired from Grace-Davison Catalysts as Davicat® AL 2400, AL 2100, and SITI 4350. AlPO-18 and SAPO-18 were synthesized hydrothermally by the method of Chen et al. [12]. The 15% WO_3/ZrO_2 catalyst, provided by ExxonMobil, was prepared by incipient wetness impregnation (IWI). The 10% MoO_3/SiO_2 stabilized with <1% K_2O was provided by Ferro and also was prepared by IWI. The HZSM-5 is an MFI zeolite (Si/Al = 21.5, PQ Corp.) characterized by Dooley et al. [13].

Table 1 BET surface areas of catalysts

Composition	Surface area (m^2/g)
γ-Al_2O_3	170
4% La_2O_3/Al_2O_3	325
3% TiO_2/SiO_2	350
15% WO_3/ZrO_2	78
10% WO_3/Al_2O_3	161
<1% K_2O/10% MoO_3/SiO_2	243
HZSM-5 (Si/Al = 21.5)	443
SAPO-18 (Al/Si = 10)	466

The 10% WO_3/Al_2O_3 catalyst was prepared by IWI from Conoco Catapal alumina using a 22 wt% $Na_2WO_4 \cdot 2H_2O$ solution. After IWI the solid product was refluxed with 1.5 times excess concentrated HCl, initially added dropwise. The reaction $Na_2WO_4 \cdot 2H_2O + 2HCl \rightarrow WO_3 + 3H_2O + 2NaCl$ takes place under these conditions. An excess of 5% NH_4NO_3 was then added to react any excess HCl to NH_4Cl, and the solid was then washed with DI water followed by drying at 120 °C.

Fixed bed reactor experiments were carried out using 1.5–2.5 g of catalyst. Methanol (Fisher, HPLC) was mixed with 12.0% H_2S/N_2 (Gas Analytical Services, certified standard) in a capillary tube vaporizer at 200 °C. The weight hourly space velocity of methanol (WHSV) was varied between 0.07 and 1.6 g/h-g cat., the molar feed ratio of methanol to H_2S from 0.3 to 2.2, and the reactor temperature from 360 to 400 °C. The pressure at the reactor inlet was 1.3–1.7 bar. Catalysts were calcined in nitrogen or air prior to use at 400–500 °C and regenerated in air in the same temperature range after extensive use. The composition of the reactor effluent was analyzed by an HP 5890 Series II GC with a Zebron ZB-1 column and a flame ionization detector.

The acidic properties of the catalysts were characterized by thermal analysis of 1-propanamine (1-PA) desorption using the method of Kanazirev et al. [14]. A Perkin-Elmer TGA7 microbalance was used to detect weight change upon thermal treatment of the catalysts in He or a mixture of He and 1-PA. About 10–15 mg of sample was placed in a platinum microbalance pan and dried in 50 cm^3/min He flow from 50 to 400 °C at 10 °C/min, with a final hold of 10 min or more. The sample was then rapidly cooled to 50 °C, then exposed to 1-PA until saturated, bubbling 50 cm^3/min He through the 1-PA at ambient temperature. The bubbler was then bypassed and the sample purged with He for 10 min at 50 °C. Thermogravimetric analysis was performed by ramping the temperature from 50 to 550 °C at 5 °C/min.

3 Results

In the following discussion, yield (MT, DMS, DME) is the molar percentage of methanol fed to the reactor that reacts to a given product. Sulfur product yield is the sum of the MT and DMS yields, and the selectivity to MT or DMS is defined as the molar percentage of methanol forming that product. All yields and selectivities represent an average of at least three data points at steady-state conditions. The affinity for a reaction (A) is equal to $-\Delta G/RT$, where ΔG is the Gibbs free energy of the reaction based on conditions (temperature and composition) at the reactor exit [15]. Details of the thermodynamic calculations of ΔG, ΔH, and equilibrium compositions of mixtures leaving the reactor can be found in a thesis [16]. Standard calculations of the Weisz–Prater modulus showed that it was $<10^{-2}$ for all catalysts under all conditions, and therefore it can be concluded that the kinetics results were unaffected by mass transfer effects [17]. Details of these calculations can also be found in a thesis [16].

La_2O_3/Al_2O_3 gave high yields to sulfur products even at high space velocities. At a temperature of 400 °C, methanol space velocities of 38–135 μmol/(m^2 h), and a feed ratio (moles MeOH/moles H_2S) of 1.9–2.1, 92–97% of the methanol was converted to sulfur products with a selectivity to DMS between 89 and 96%. Examining Table 2, it can be seen that the selectivity to DMS increased with temperature, increased with feed ratio over a range of 1.4–2.1, and decreased only slightly with respect to space velocity.

Figure 1 shows how the product distribution varied with increasing conversion of methanol to sulfur products. The solid curves represent calculated values (at 370 °C) of methanol conversion, and DME, DMS and MT yields, that result from allowing reactions (3) and (4) to come to equilibrium while holding the extents of reactions (1) and (2) constant. In other words, the total sulfur product yield is held constant, while DMS, MT and DME are allowed to equilibrate according to reactions (3) and (4). For the sulfur product yields observed here, the equilibrium curves do not vary significantly with temperature over the range 340–400 °C, so an average temperature of 370 °C was used to construct the figure. The sulfur product distributions do change with respect to feed ratio; for DMS and MT, curves are constructed at feed ratios of 1.6 (lower curve for DMS and upper curve for MT) and 2.0. With respect to feed ratio, the equilibrium DMS yield at a given sulfur product yield increases, the equilibrium MT yield decreases.

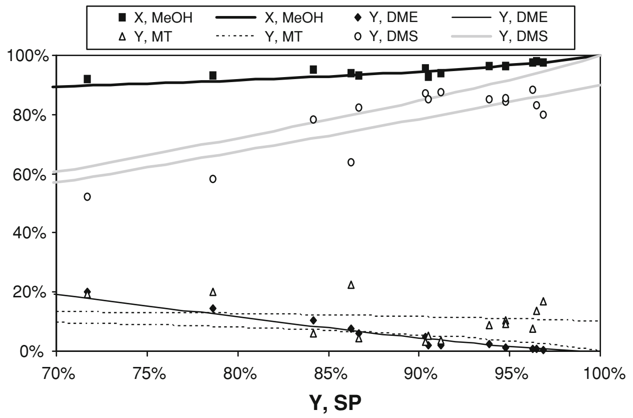

Fig. 1 Yields and conversions with La_2O_3/Al_2O_3 versus yield to sulfur products (Y, SP, the sum of the yields to DMS and MT) at 340–400 °C. The equilibrium curves are drawn for feed ratios of 1.6 and 2.0. For DMS yield at equilibrium, feed ratio = 1.6 for *bottom curve*; for MT yield at equilibrium, feed ratio = 2.0 for *bottom curve*

As shown in Fig. 1, the conversion of methanol to DME peaked at residence times shorter than investigated here. The yield to sulfur products increased from 72 to 97%, while the conversion of methanol increased only from 92 to 98%. The yield to DME decreased from 20 to 1% over the same range. From Fig. 1 we see that DME remains close to equilibrium; affinity calculations confirmed this. We can conclude that at longer residence times the DME converts back to methanol or adsorbed methoxy, which subsequently react to form sulfur products.

At 400 °C and an H_2S conversion <99%, the affinity of reaction (4) is close to zero, indicating that this reaction is close to equilibrium. The affinity of (4) decreases with temperature from 340 to 400 °C. The average yield to

Table 2 Performance of La_2O_3/Al_2O_3 with increasing feed ratio, at 400 °C. To convert to WHSV, divide space velocities by 96

Feed ratio	μmol/(m^2 h)	X, MeOH	X, H_2S	Y, SP[a]	S, MT	*A*
1.4 ± 0.7	31 ± 14	98 ± 2	78 ± 27	97 ± 3	14 ± 20	−0.1 ± 0.7
1.7 ± 0.1	68 ± 5	94 ± 3	82 ± 4	91 ± 5	4 ± 2	−2.5 ± 1.0
1.7 ± 0.04	138 ± 3	98 ± 1	99 ± 1	97 ± 1	17 ± 1	3.6 ± 1.1
1.9 ± 0.09	134 ± 6	96 ± 1	99 ± 1	95 ± 1	11 ± 2	2.3 ± 0.1
1.9 ± 0.06	84 ± 3	97 ± 1	99 ± 2	96 ± 1	8 ± 2	1.7[b]
1.9 ± 0.06	135 ± 4	96 ± 1	99 ± 1	95 ± 2	10 ± 1	3.0 ± 0.3
1.9 ± 0.08	77 ± 3	97 ± 1	99 ± 1	94 ± 2	9 ± 3	2.5[b]
2.0 ± 0.1	38 ± 2	96 ± 2	93 ± 1	90 ± 4	4 ± 2	−1.4 ± 1.0
2.0 ± 0.08	79 ± 3	99 ± 1	97 ± 2	91 ± 2	6 ± 3	0.3 ± 1.6
2.1 ± 0.3	360 ± 50	93 ± 1	102 ± 4	79 ± 6	26 ± 4	
2.1 ± 0.1	82 ± 4	93 ± 1	96 ± 1	87 ± 3	5 ± 2	−0.2 ± 0.9

[a] Total methanol yield to all sulfur products

[b] Some indeterminate (infinite) values of *A*

DMS (when fit by linear regression) increases from 55 to 89% as the sulfur product yield increases from 72 to 97%. The average MT yield decreases somewhat, to be more in line with the equilibrium predictions (Fig. 1).

At 340 °C, WO_3/ZrO_2 converts >84% of the methanol to sulfur products at space velocities between 107 and 272 μmol/(m^2 h) and feed ratios of 1.3–2.2; e.g., at 262 μmol/m^2-h and a feed ratio of 2.0–2.1, 85% of the methanol is converted to sulfur products. On La_2O_3/Al_2O_3 at the same temperature and a similar feed ratio, only 72% of the methanol is converted to sulfur products at a space velocity of only 40 μmol/(m^2 h), so clearly WO_3/ZrO_2 is more active. At 360 °C, WO_3/ZrO_2 converted 1.6–2.0% of the methanol to hydrocarbons, so temperatures above 360 °C were not examined. As with La_2O_3/Al_2O_3, the selectivity to DMS increased by 3–5% when the temperature was increased from 340 to 360 °C. This selectivity decreased with space velocity while increasing with feed ratio.

As seen in Fig. 2, the yields to total sulfur products and DME behaved in the same way at longer residence times as for La_2O_3/Al_2O_3. At sulfur product yields >80%, the affinity for reaction (3) is less than −2, in agreement with the small amount of DME actually observed at these conditions. As the yield to sulfur products increased from 77 to 99%, the average DMS yield increased from 70 to 83%. But unlike La_2O_3/Al_2O_3, the MT yield also increased significantly, from 7 to 15%. In other words, there was more preference for MT with this catalyst. At 340 °C, the affinity of reaction (4) is positive for most conditions. We conclude that operation at 340–360 °C, necessitated by the reactions of DME to hydrocarbons at higher temperatures, limits the rate of disproportionation of MT and so the DMS yield.

The trends in results for a simple γ-Al_2O_3 catalyst were similar to those of the previous two catalysts, but the activity is lower. At a temperature of 400 °C and a feed ratio of 2.0–2.1, 86% conversion of methanol to sulfur products was observed at a space velocity of 32 μmol/(m^2 h). At the same temperature and a similar feed ratio on La_2O_3/Al_2O_3, the conversion was 91% at a space velocity of 79. At 340 °C and a feed ratio of 2.3–2.4, the γ-Al_2O_3 catalyst converted 57% of the methanol to sulfur products at 89 μmol/(m^2 h), compared to 79% at 167 μmol/(m^2 h) for WO_3/ZrO_2 at comparable conditions. As with the other two catalysts, the selectivity to DMS increased with temperature, decreased with space velocity, and increased slightly with feed ratio.

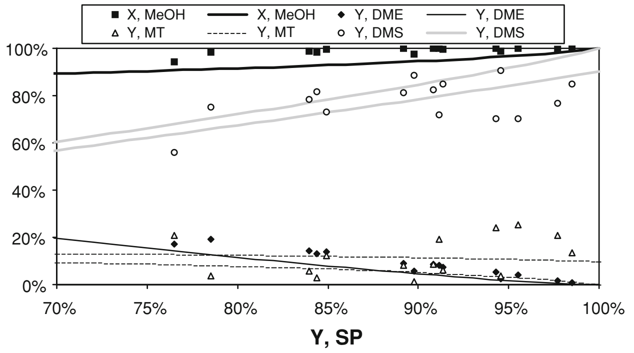

Fig. 2 Yields and conversion on WO_3/ZrO_2 versus yield to sulfur products (Y, SP) at 340 °C. The equilibrium lines have the same meaning as in Fig. 1

Trends in methanol conversions and DME yields versus sulfur product yields for γ-Al_2O_3 were also similar to those of the previous two catalysts. Under all conditions investigated, the affinity for reaction to DME was close to equilibrium ($-1 < A < 0$). The affinity for reaction (4) was negative, indicating that this reaction produces MT from DMS near the reactor exit. Nonetheless, the DMS yield increased with methanol conversion while the MT yield remained relatively constant. Therefore the rate of the serial reaction to DMS (reaction 2) on this catalyst is fast.

HZSM-5 was the least active of the four catalysts giving high DMS yields. Compared to γ-Al_2O_3 at 400 °C and a feed ratio of 1.7–1.8, 77% of the methanol was converted to sulfur products over HZSM-5 at a space velocity of 26 μmol/(m^2 h), compared to 94% for γ-Al_2O_3 at the same conditions. However, HZSM-5 was the least selective catalyst to MT, giving <5% MT at 400 °C, for most conditions. Just as for the other catalysts in this group, the selectivity to DMS increased somewhat with temperature and decreased with space velocity. But unlike the others in the group, the selectivity to DMS decreased slightly (3–4%) with increasing feed ratio (1.8:2.0). The increases in DMS were mostly at the expense of DME. At the lower sulfur product yields (50–65%), the yield of DME was constant and the affinity for its production positive. But at higher sulfur yields, the yield to DME closely following the predicted equilibrium curve, with calculated affinity close to zero. Like the γ-Al_2O_3 catalyst, the affinity for MT disproportionation is negative, so MT was produced from DMS near the reactor exit. Nevertheless the observed yields to DMS increased and to MT decreased or remained constant as methanol conversion increased from 70 to 90% (Fig. 3).

WO_3/Al_2O_3 was the most selective catalyst to MT examined; reaction results are shown in Fig. 4. Over a wide range of conditions, with feed ratios between 0.3 and 0.7, the selectivity to MT was >80%. Temperatures from 340 to 400 °C and space velocities from 14 to 59 μmol/(m^2 h) were investigated. Under all conditions, increasing the temperature or feed ratio or decreasing the space velocity decreased the MT selectivity. The highest observed selectivity to MT (93%) was obtained at 340 °C, a feed ratio of 0.33 and a space velocity of 74 μmol/(m^2 h). But even

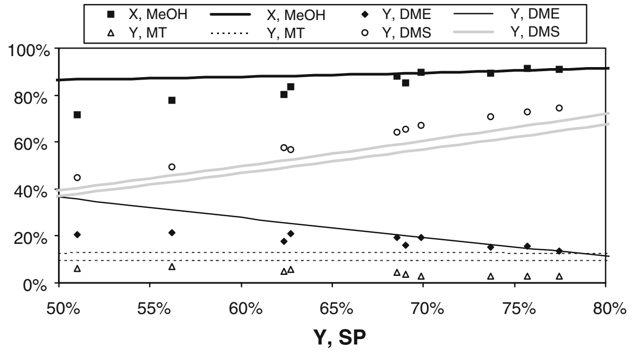

Fig. 3 Yields and conversion on HZSM-5 versus yield to sulfur products (Y, SP) at 340–400 °C. The equilibrium lines have the same meaning as in Fig. 1

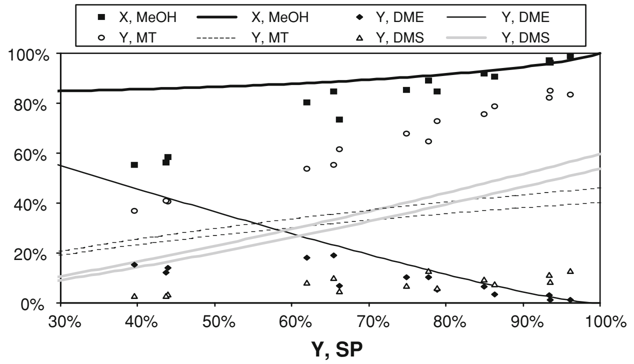

Fig. 4 Yields and conversion on WO_3/Al_2O_3 versus yield to sulfur products (Y, SP) at 340–400 °C. Equilibrium lines have same meaning as in Fig. 1 but are drawn at feed ratios of 0.3 (*lower curve*, DMS and *upper curve*, MT) and 0.4

under more extreme conditions −400 °C, feed ratio 0.31, space velocity 26 μmol/(m^2 h), 94% sulfur product yield −MT still comprised 91% of the sulfur products.

At sulfur product yields <90%, the affinity for DME production is positive; at higher sulfur product yields the DME and methanol are closer to equilibrium. As the sulfur product yield increased from 40 to 96%, the DME yield decreased from 17 to 1% and the methanol conversion increased from 55 to 99%. Both DMS and MT yields increased with methanol conversion in the range 50–100% (Fig. 4), but in general the DME–MT–DMS distribution is far from equilibrium conditions for the reaction set (1), (2), (3), (4).

At temperatures from 340 to 400 °C, a feed ratio of 0.3–0.4, and space velocities from 6 to 8 μmol/(m^2 h) (WHSV 0.05–0.06), MoO_3/SiO_2 produced MT at a selectivity of 60–80%. As the temperature increased over this range, the sulfur product yield varied from 45 to 68%, being highest at 360 °C. Carbonyl sulfide is produced in varying amounts and increased from 3 to 53% over this temperature range. Carbon disulfide and ethanethiol were also produced, and their yields also increased with temperature.

SAPO-18 and AlPO-18 were chosen to match the effective pore diameter of the catalyst (~3.8 Å for these materials) to the molecular diameter of DMS (4.1 Å) in an attempt to attain shape selectivity to this product. However, both catalysts make mostly DME. At 360–400 °C, the SAPO-18 catalyst converted 6–43% of the methanol to sulfur products at feed ratios of 1.0–2.2 and space velocities of 32–39 μmol/(m^2 h). When the sulfur product yield was 6%, the MT selectivity was 63%, decreasing to 11% at 43% yield. At a sulfur product yield of 6, 86% of the methanol had been converted to DME. The sulfur product yield increased with decreasing space velocity and increasing temperature, but the methanol conversion remained constant at 94–95%. At higher temperatures and feed ratios, the catalysts became very active for C3–C4 olefins after being on stream for about an hour. But after regeneration, this activity disappeared and the original activity was restored.

AlPO-18 was even less active to sulfur products, but more selective to DMS, than SAPO-18. The highest yield to sulfur products was 32% at 400 °C, a feed ratio of 2.9 and a space velocity of 16 μmol/m^2 h. The behavior of the reaction to DME was similar to that of SAPO-18.

Less than 1% of the methanol was converted to sulfur products by TiO_2/SiO_2, making it the least active catalyst studied. Reaction conditions were: 400 °C, a feed ratio of 2.5 and a space velocity of 21 μmol/m^2 h. Some DME was produced.

To quantify deactivation, catalysts were kept on stream for 2 days, 8–10 h a day, at typical operating conditions. After this, the catalysts were regenerated overnight in 20–50 mL/min of air (STP) at 400 °C for the mixed metal oxides and 500 °C for HZSM-5 (whose thermal stability is greater). La_2O_3/Al_2O_3 and γ-Al_2O_3 showed no signs of deactivation over the 2-day period. HZSM-5 and WO_3/Al_2O_3 lost about 8% of their initial DMS/MT yield but were completely regenerated. WO_3/ZrO_2 lost about 10% DMS yield but was regenerated to within 5% of the original yield. The deactivation behavior of the other catalysts was not examined because they were not suitable for either DMS or MT production.

Data from the 1-propanamine adsorption/desorption TGA experiments were normalized to the weight of the dry catalyst and the time derivative of weight was determined. By analyzing the derivative, the distribution of acid site strengths could be approximated, assuming that desorption of 1-propanamine or its Hoffmann elimination products propene and ammonia occurs on stronger sites at higher temperatures [14]. It should be noted that this method does not distinguish between Lewis and Bronsted centers, since 1-propanamine can adsorb on both types of sites. All of the samples that were analyzed showed a low temperature desorption peak located between 50 and 150 °C, while

HZSM-5, SAPO-18 and WO_3/ZrO_2 showed other peaks located between 250 and 400 °C. Any propanamine that did not desorb below 400 °C was considered to be bound to strong acid sites that would definitely catalyze the elimination reaction, based on previous studies [14]. All the catalysts contained 2–6 µmol/m^2 of weak sites characterized by desorption below 200 °C. TiO_2/SiO_2 showed almost no sites desorbing above 150 °C, and was almost completely inactive. Furthermore, the other catalysts showing low activity had a large number of sites between 150 and 200 °C, so we conclude that weak sites characterized by propanamine desorption below 200 °C are inactive for methanol-H_2S reactions.

The number of acid sites of each catalyst that desorb 1-propanamine or its Hoffmann elimination products (propene and NH_3) at >200 °C is shown in Fig. 5. Comparing the γ-Al_2O_3, La_2O_3/Al_2O_3, WO_3/ZrO_2, and HZSM-5 catalysts, it can be seen that they all have roughly the same number of such sites between 200 and 400 °C, 1–2 µmol/m^2. Roughly 0.5 µmol/m^2 of sites are characteristic of both the 200–250 °C and 250–300 °C ranges, although γ-Al_2O_3 has slightly fewer (0.4 µmol/m^2) in each range. For HZSM-5, the desorption peak located in this region was found to arise from the desorption of one molecule of 1-propanamine from an acid site where two were initially adsorbed [14]. Because there is no Hoffmann elimination associated with this desorption, and because the catalysts all exhibited similar desorption behavior, we conclude that the concentration of sites in the 200–300 °C range does not correlate with reactivity to the desired sulfur products.

Among the four active (to DMS) catalysts, the number of sites in the 300–350 °C regime varied from 0.3 to 0.5 µmol/m^2, decreasing in the order $WO_3/ZrO_2 > La_2O_3/Al_2O_3 > \gamma$-$Al_2O_3 >$ HZSM-5. This is the same order as found for the activity of these catalysts to make desired sulfur products. We conclude that sites desorbing in this range are the most active for DMS production. The number of sites in the 350–400 °C range is between 0.2 and 0.6 µmol/m^2, decreasing in the order HZSM-5 $> WO_3/ZrO_2 > La_2O_3/Al_2O_3 > \gamma$-$Al_2O_3$. WO_3/ZrO_2 showed a desorption peak centered in this region while for HZSM-5 a desorption peak began in this region. Of this group, only HZSM-5 retains the reaction products of 1-propanamine at above 400 °C, at a concentration of 1.0 µmol/m^2. We conclude that sites desorbing 1-propanamine at >350 °C are in general too strong to participate in the reaction to DMS, although they cannot be categorically excluded based on this evidence.

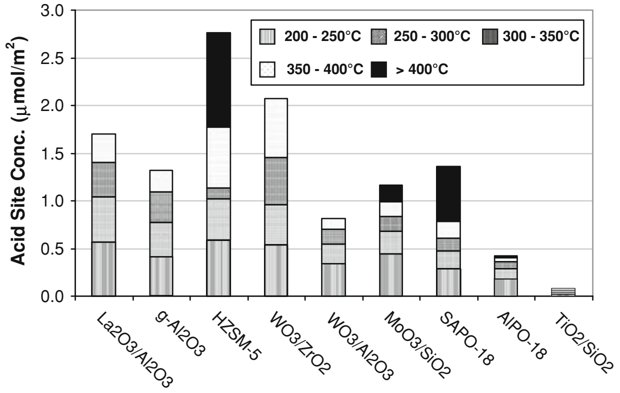

Fig. 5 Concentration of acid sites determined by the desorption of 1-propanamine in different temperature ranges

The group of catalysts WO_3/Al_2O_3, MoO_3/SiO_2, SAPO-18, and AlPO-18 have fewer sites desorbing between 200 and 400 °C, ranging from 0.4 to 1.0 mmol/m^2. The number of sites desorbing between 200 and 300 °C ranges from 0.3 to 0.7 mmol/m^2 and decreases in the order $MoO_3/SiO_2 > WO_3/Al_2O_3 >$ SAPO-18 > AlPO-18. These sites make up a larger fraction of the 200–400 °C sites than for the previous group of four catalysts (60–70% compared with 50–60%). The number of sites desorbing from 300 to 350 °C ranges from 0.1 to 0.2 mmol/m^2, decreasing in the order $MoO_3/SiO_2 \sim WO_3/Al_2O_3 >$ SAPO-18 > AlPO-18. Except for MoO_3/SiO_2, this follows the order of activity of these catalysts towards sulfur products. The number of sites desorbing from 350 to 400 °C lies in the same range and decreases in the order SAPO-18 $> MoO_3/SiO_2 > WO_3/Al_2O_3 >$ AlPO-18. SAPO-18, and MoO_3/SiO_2 both retained reaction products of 1-propanamine at above 400 °C, 0.6 and 0.2 mmol/m^2 of propanamine, respectively. Taken together, these data suggest that for the second group of catalysts the 300–350 °C desorption range is also the most relevant. While WO_3/Al_2O_3 was more active than MoO_3/SiO_2, the completely different nature of the latter—it is both a dehydrogenation and condensation catalyst—renders comparisons based on simple acid strength measurements tenuous.

4 Discussion

The catalysts fell into three groups based on activity. The first group, consisting of La_2O_3/Al_2O_3, γ-Al_2O_3, HZSM-5, and WO_3/ZrO_2, showed much higher activity to sulfur products. Although the catalysts in this group were not investigated under identical conditions of temperature and feed ratio, we can conclude that the order of specific activity (on a surface area basis) is $WO_3/ZrO_2 > La_2O_3/Al_2O_3 > \gamma$-$Al_2O_3 >$ HZSM-5. As seen above, the catalyst behavior over a wide range of conditions could be correlated in terms a single parameter, the total sulfur product yield. The second group of catalysts consisted of WO_3/Al_2O_3, MoO_3/SiO_2, SAPO-18, and AlPO-18. These were less active for sulfidation than the first group, but generally more selective to MT.

The first group is selective for DMS production. WO_3/ZrO_2 was not suitable at >340 °C due to hydrocarbon formation. At 400 °C, the activities of the other three catalysts decreased in the order $La_2O_3/Al_2O_3 > \gamma\text{-}Al_2O_3 >$ HZSM-5, and the yield to hydrocarbons was >1%. Conditions could be found for all of these, except HZSM-5 (340 °C for WO_3/ZrO_2, 400 °C for La_2O_3/Al_2O_3, and $\gamma\text{-}Al_2O_3$), at which more than 90% of the methanol was converted to sulfur products. At such conditions, the selectivity to MT was <10% for molar feed ratios of methanol to H_2S >1.8. For HZSM-5, >75% sulfur product yield was achieved, along with an MT selectivity <5%, at optimal conditions.

On all of these catalysts, the MT yield decreased slightly or remained constant with respect to increased contact time, while the DMS yield increased. The compositions of both sulfur products and of DME were close to the equilibrium values calculated at a fixed total sulfur product yield. These observations are inconsistent with a purely serial mechanism to DMS (MeOH → MT → DMS), instead suggesting that MT disproportionation is fast and often close to equilibrium (affinity for reaction (4) near zero). Since the disproportionation reaction is fast, MT in the product stream can be separated and recycled to the reactor feed stream.

For all four of these catalysts, the DME yield decreased with contact time, with DME decomposing mainly to sulfur products. For La_2O_3/Al_2O_3 and $\gamma\text{-}Al_2O_3$, DME and methanol are close to their equilibrium concentrations at a fixed yield of sulfur products. For WO_3/ZrO_2, the DME yield is slightly greater than its calculated equilibrium value; for HZSM-5 it is slightly less. Therefore, DME can also be separated and recycled to the feed, to be converted to DMS.

Characterization of the acid sites on these catalysts by thermal desorption of 1-propanamine suggests that sites desorbing the Hoffmann elimination products of 1-PA (propene and NH_3) in the range of 300–350 °C are responsible for most of the activity to sulfur products. This is typically the range where the elimination products desorb from catalysts with more moderate-to-strong Lewis (than Bronsted) acid sites [14]. The number of sites in this range for these materials decreases in the same order as the catalytic activity ($WO_3/ZrO_2 > La_2O_3/Al_2O_3 > \gamma\text{-}Al_2O_3 >$ HZSM-5). HZSM-5 was the only catalyst of this group to retain the reaction products of 1-PA above 400 °C, and it is the poorest sulfidation catalyst. The relationship between sulfur product formation and acid sites in the 300–350 °C desorption range also holds up for the other catalysts that are not members of this group. Some anomalies exist—e.g., H-ZSM-5 is more active than WO_3/Al_2O_3, but has a small number of sites desorbing from 300 to 350 °C; MoO_3/SiO_2 is less active for sulfidation than WO_3/Al_2O_3, but their site populations in the 300–350 °C range are similar. But H-ZSM-5 also has an unusually large number of sites desorbing from 350 to 400 °C (see Fig. 5), and the sites at the lower end of this temperature range were probably active for sulfur product formation. As for MoO_3/SiO_2, its significant dehydrogenation activity to COS (not found for any other catalyst used here) skews its behavior in an acid site-activity correlation.

The WO_3/Al_2O_3 was active and selective to MT, with DMS selectivity <15%. Yields to sulfur products >90% could be achieved only at low space velocities ($\sim$15 μmol/(m^2 h)), so WO_3/Al_2O_3 is less active than the four catalysts in the first group. Yields to MT and DMS were far from calculated equilibrium values, indicating that the disproportionation reaction is slower. The DME yield is slightly below its calculated equilibrium value at a given sulfur product yield, and decreases with contact time, suggesting that the methanol condensation to DME is still fast. Therefore, DME can be recycled here as well.

For all of the catalysts discussed above, the selectivity to sulfur products does not decrease as the partial pressure of methanol decreases by at least an order of magnitude. This indicates that the rate of methanol-H_2S condensation is close to zero order in methanol.

The other catalysts that were studied (Mo_3/SiO_2, TiO_2/SiO_2, SAPO-18, and AlPO-18) were unsuitable for MT or DMS production. Mo_3/SiO_2 had low selectivity to sulfur products and produced a large amount of carbonyl sulfide, CS_2 and other dehydrogenation products. SAPO-18 and AlPO-18 had low activity except to DME; TiO_2/SiO_2 had almost no activity.

Based on experimental results in this and previous work, along with the catalytic chemistry associated with these metal oxides, a surface reaction pathway emerges that explains the activity of the catalysts in the sulfidation of methanol and the distribution of products. The sulfidation activity is highest for catalysts with Lewis centers of modest strength (Q_{CO} of 30–40 kJ/mol) [2]. Alumina falls in this range and the activity sharply decreases when the Al cation is replaced with a neighboring element from the periodic table (either Mg or Si). It is also apparent that slightly basic catalysts are selective to MT, while more acidic catalysts favor DMS.

In order to postulate a pathway consistent with these trends, the adsorbate coverage of the catalyst surface must first be considered. If it is assumed that dissociative adsorption of methanol and H_2S is not rate limiting, then the surface should be in equilibrium with these two components and also with H_2O in the gas phase. Certainly this is a reasonable assumption for methanol given its zero-order kinetics behavior. Furthermore, methanol and water have roughly the same adsorption energy on a Lewis acid/base center pair, because the O–H bonds that are broken in the adsorption of both molecules are of similar acidity. As discussed below, H_2O has a higher adsorption energy on alumina than does H_2S. So at low conversions, methanol should be the most abundant surface species, and at high conversions, water.

Ab-initio calculations were performed in this work using Gaussian 03 [18] to confirm the difference in binding energies of hydroxyl and bisulfide species with a Lewis center. Clusters consisted of a cation (Na^+, Mg^{2+}, Al^{3+}, and Si^{4+}) coordinated to O^{2-} and OH^- ligands. Clusters were optimized using the B3LYP density functional and the 6-31G basis set and energies were calculated using the 6-311G(d) basis set. The same calculation was performed on a cluster with one OH^- ligand replaced by an SH^- ligand. It was found that for Al^{3+} and Si^{4+}, H_2O was bound more strongly than H_2S by about 30 kJ/mol. On Na^+ and Mg^{2+}, H_2S was bound more strongly by 23 and 8 kJ/mol, respectively. For alumina therefore H_2S coverage should be well below monolayer, but H_2S coverage should increase with catalyst basicity beyond pure Al_2O_3.

The surface acidity/basicity directly affects surface bond strengths. For acidic catalysts, the valence band energy is low and the negatively charged species (oxygen and sulfur) are more strongly bound to the lattice than they are to the positively charged surface species (protons and methyl groups) [19]. As the surface becomes basic, this trend reverses; the binding of surface oxygen and sulfur atoms with the lattice weakens, and their binding to protons and methyl groups strengthens. For this reason the reactivity of surface protons and methyl groups increases with acid strength; the reactivity of adsorbed sulfur and oxygen follows the opposite trend.

Ab-initio calculations using Gaussian 03 [18] were performed for H_2S, H_2O, MT, MeOH, DMS, and DME to determine heterolytic bond dissociation energies. Structure optimization and energy calculations of the molecules and ions were done using the B3LYP density functional and the 6-311 + G(d) basis set. The bond energy decreased in the order O–H (1,610–1,640 kJ/mol) > S–H (1,470–1,500 kJ/mol) > C–O (1,160–1,180 kJ/mol) > C–S (1,040–1,070 kJ/mol).

In the simplified pathway proposed (Fig. 6), it is assumed that the transfer of a methyl group between two surface atoms is slower than the analogous transfer of a proton. Therefore, methyl transfer is the rate determining step of each overall reaction. The activation barrier for the process is affected by both the binding energy of the methyl group to the surface and the binding energy of the electron donor atom (oxygen or sulfur) to the surface. Since methyl groups are bound more weakly on acidic surfaces and the sulfur and oxygen atoms are bound more weakly on basic surfaces, it is expected that the activation barrier for sulfidation is lowest somewhere in the middle of a suitable acidity scale (for example, one related to Q_{CO} or to the desorption temperature of 1-PA and its Hoffmann elimination products). At greater acid strengths, the increase in oxygen and sulfur binding energy increases the barrier height for sulfidation [5]. At lesser acid strengths, the increased binding energy of the methyl groups increases the barrier height. This finding is confirmed experimentally in that more acidic oxide catalysts than used here (e.g., PO_4^{3-}/SiO_2, silica-aluminas, $Nb_2O_5 \cdot nH_2O$), and more basic oxide catalysts than used here (MgO, Na-Y, Cs/Al_2O_3, K/Al_2O_3) are in both cases far less active for the sulfidation of methanol [2, 7, 8, 11, 20, 21]. It is also reflected in the finding that chemisorbed methanol is most reactive on catalysts that are neither strongly basic nor strongly acidic, such as alumina and La_2O_3/Al_2O_3. The good correlation between the

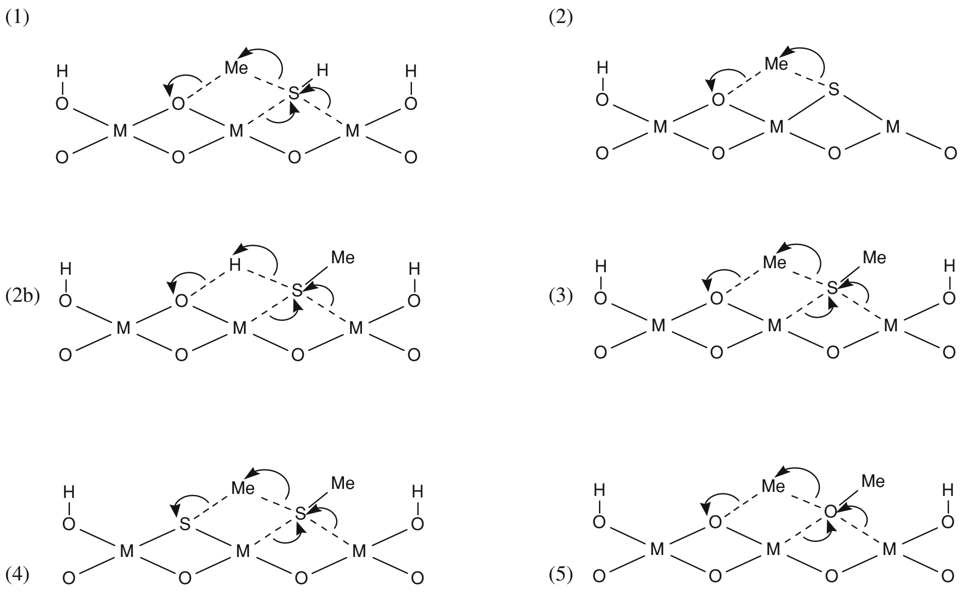

Fig. 6 Steps of proposed surface reaction pathways. M is a metal cation acting as a Lewis acid site

desorption of 1-PA in the 300–350 °C range is another argument in favor of intermediate acid strength leading to maximum sulfidation activity; a good counterexample is the behavior of the SAPO-18 (here) and PO_4^{3-}/SiO_2, [2] where a high ratio of strong/moderate acid sites led to mostly DME.

We can also refer to two previous studies correlating sulfidation activity and acid site distribution [21, 22]. The first of these assumed that Lewis acid/base pairs were responsible for activity, estimated the strength of such pairs from the composition, and concluded that stronger acidity was required for DMS (vs. MT) production. This study was restricted to a narrower range of catalysts, doped MCM-41 silicas, and there was no independent measurement of acid strengths. The second study was at conditions closer to ours, using a wider range of catalysts supported on SiO_2, Al_2O_3, and Nb_2O_5, with the activity for propanol dehydration as the measure of acid strength. Most of the catalysts were too basic to give high sulfur compound yields, but an increase in the strength of basic sites beyond Al_2O_3 resulted in lower overall activity and higher selectivity to MT, while a catalyst of high Lewis acid strength ($Nb_2O_5 \cdot nH_2O$) also gave a lower sulfur product yield. In both studies the broad conclusions agree with our own, but a problem in direct comparisons is that in both the methanol conversion was not on a common basis (in our study, activity comparisons were typically made at >90% methanol conversion), and as seen low methanol conversions result in large amounts of primary product DME, clouding the interpretations.

So we postulate that the surface reaction pathway on alumina begins with the dissociative adsorption of methanol and H_2S onto LC/BC (Lewis acid–base) pairs. The resulting bisulfide (LC-SH) and methoxy (LC-Me) groups can then react according to several different paths as shown in Fig. 6. If a methyl with slight positive charge is adjacent to the bisulfide, the two can combine and desorb as MT (1), leaving a regenerated LC/BC pair. Alternatively, the bisulfide hydrogen can desorb by combining with a neighboring hydroxyl or methoxy group to form water or methanol, resulting in a sulfide (LC-S) and LC on the surface. The sulfide is expected to be more reactive than the bisulfide, and a neighboring methyl group can transfer to it to form a mercaptide species (2). The mercaptide (LC-S-Me) can then be protonated by a neighboring hydroxyl and desorb as MT (2b). Both of these paths should be first order in H_2S and irreversible. Because the surface coverage by methanol is expected to be high at low conversion, the kinetics of these pathways should be less than first order in methanol, as observed.

Once formed, MT dissociatively adsorbs onto LC/BC pairs in a way similar to H_2S and will react with other surface species. The adsorbed mercaptide can react with a neighboring methyl species and desorb as DMS (3). This reaction is expected to be first order in MT and irreversible. The disproportionation reaction will also occur to produce DMS and H_2S from MT. This reaction can occur when a methyl group is transferred from one surface mercaptide to another to desorb DMS (4), leaving a sulfide and LC on the surface. This reaction is similar to (3), but should have a lower activation barrier, because the methyl group that is transferred is more weakly bound to sulfur than it is to oxygen. This path is reversible and expected to be second order in MT. A diagram of paths 1–4 is shown in Fig. 7. In a reaction similar to (4), a methyl group can transfer between two neighboring methoxy groups to desorb DME (5), this path being fast and reversible.

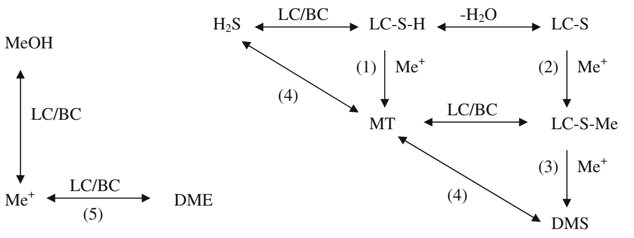

Fig. 7 Diagram showing the relations between paths 1–5 in the overall reactions. 0020LC represents a Lewis center, BC a basic center, Me^+ a methyl group (of a methoxy ligand) with a partial positive charge

Insight into the effects of surface acid strength on the proposed pathways can be gained from the trends in activity and selectivity of the experimental data. As mentioned earlier, the rate-determining step of each path will have a minimum activation barrier at a certain level of surface acid strength. The activation barrier heights for the reaction paths leading to either DMS or MT appear to be lowest at acid strengths close to that of γ-Al_2O_3, however, the minimum barrier height of path 3 occurs at higher acid strength (than Al_2O_3)—compare the selectivity results for La_2O_3/Al_2O_3 (more acid sites in the 300–350 °C desorption range) to WO_3/Al_2O_3. This suggests that transferring the second methyl group to a sulfur atom to form DMS is more difficult than transferring the first methyl group to form MT, and requires stronger acid sites.

5 Conclusions

- Oxides with acid sites of intermediate strength (desorbing the products of the Hoffmann elimination of 1-propanamine from 300 to 350 °C) are good catalysts for the condensation of methanol and H_2S to DMS. Oxides with a smaller concentration of these sites, but without many strong sites (e.g., WO_3/Al_2O_3), are better for the production of MT.

- The behavior of good sulfidation catalysts over wide ranges of temperature, feed molar ratio and space velocity can be correlated in terms of the total sulfur product yield. The product distribution is characterized by the disproportionation reaction of MT and the condensation to DME being both close to equilibrium.
- The sulfidation reactions of methanol are close to zero order in methanol, for good sulfidation catalysts.
- The selectivity to MT decreases with increasing feed ratio, temperature, and contact time.
- The transfer of the second methyl group to an adsorbed sulfur atom to form DMS has a slightly higher energy barrier than the transfer of the first methyl group to form MT, requiring stronger acid sites.

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