ZEOLITE AND METAL OXIDE CATALYSTS FOR THE PRODUCTION OF DIMETHYL SULFIDE AND METHANETHIOL

By Kerry M. Dooley*, and Craig P. Plaisance
Dept. of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803
*To whom correspondence should be addressed, dooley@lsu.edu

ABSTRACT

Metal oxide and zeolite catalysts were examined to determine their suitability for the production of methanethiol and dimethyl sulfide from the condensation of methanol and hydrogen sulfide. Fixed bed reactor experiments were used to test the catalysts in these processes. The acid sites of these catalysts were characterized by investigating the thermal desorption of 1-propanamine from these sites. It was found that WO_3/ZrO_2, La_2O_3/Al_2O_3, Al_2O_3, and HZSM-5 catalysts were active and selective in the production of dimethyl sulfide. The WO_3/Al_2O_3 catalyst was less active than these four, but was selective to methanethiol. Based on this work and results in the literature, a mechanism was proposed that correlates methanethiol selectivity to catalyst acid strength.

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 → MT + H_2O and H_2S + 2 MeOH → DMS + 2 H_2O. In addition to forming sulfur products (DMS and MT), methanol condenses to dimethyl ether (DME) and can react to other minor byproducts.

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

The primary molecules involved in methanol condensation reactions are MeOH, DME, MT, DMS, H_2S, and H_2O. These molecules can be weakly activated by adsorbing associatively onto Lewis acid centers (LCs), Protic centers (PCs), and basic centers (BCs) on the catalyst surface.[2] Further activation can occur by dissociative adsorption on pairs of Lewis acid and base sites.

Several mechanisms have been proposed in the literature for the reactions between methanol and H_2S on metal oxide and zeolite surfaces. Mashkina et al.[2] propose a serial mechanism for metal oxides by which surface methyl and bisulfide (HS-LC) species interact to form MT, which then desorbs. MT can then chemisorb on LCs and react with a methyl species to form DMS. The disproportionation of two molecules of MT to DMS and H2S occurs on strong acid sites such as LCs. Mashkin et al.[1] provide further evidence for this mechanism and also propose that DME is formed when surface methyl or methoxy species interact with each other or with gas phase methanol. Other mechanisms suggest that DMS is formed by the reaction of surface methyl species with gas phase H_2S [3, 4] or the reaction of gas phase H_2S and DME [5]. The overall reactions suggest by these mechanisms are

$\mathrm{MeOH + H_2S \rightarrow MT + H_2O}$ (1)
$\mathrm{MeOH + MT \rightarrow DMS + H_2O}$ (2)
$\mathrm{2\ MeOH \rightarrow DME + H_2O}$ (3)
$\mathrm{2\ MT \rightarrow DMS + H_2S}$ (4)

Mashkina et al.[2] studied silica, alumino-silica, and alumina supports doped with transition metal oxides. They found that alumina supported catalysts were an order of magnitude more active than alumino-silica supported catalysts, which were an order of magnitude more active than silica supported catalysts. The general conclusion that can be drawn from their results is that catalysts with LCs of moderate strength, such as alumina, are the most active in this reaction, while catalysts with strong or weak LCs are less active. Additionally, basic metal oxides are selective to MT and acidic metal oxides are selective to DMS [1, 6].

Several X and Y zeolites were characterized by Ziolek et al.[5] containing different cations from the alkali series. The protonated forms of these zeolites were found to be much more active in the formation of MT and DMS than the deprotonated forms [3-5]. Other studies found that HZSM-5 was the most active zeolite for this reaction [3, 4]. Additionally, they concluded that reaction (4) is faster on zeolites than reactions (1) and (2).

The aim of this project is to identify zeolite and metal oxide catalysts that are suitable for the production of either DMS or MT and then find optimal sets of reaction parameters. Properties used to determine the suitability of catalysts included activity, selectivity toward desired products, deactivation and regeneration of the catalyst, and whether or not the side products could be recycled. Reactor parameters that were optimized for each catalyst were temperature, space velocity, and feed ratio of methanol to hydrogen sulfide. Finally, a mechanism is proposed to explain trends in the effects of catalyst acid strength on the reactivities and selectivities found in the literature and in this work.

EXPERIMENTAL

In this work ten different catalysts were used, whose properties are given in Table 1. La_2O_3/Al_2O_3, Al_2O_3, and TiO_2/SiO_2 were acquired from Davison Catalysts as Davicat® AL 2400, Davicat® AL 2100, and Davicat® SITI 4350. AlPO-18 and SAPO-18 were synthesized hydrothermally by the method of Chen et al.[7] The 15% WO_3/ZrO_2 catalyst was provided by ExxonMobil and was prepared by incipient wetness impregnation (IWI). The 10% MoO_3/SiO_2 stabilized with < 1% K_2O was provided by Ferro and prepared by IWI. The HZSM-5 is an MFI zeolite (Si/Al ratio of 21.5); it was provided by PQ Corp. and was characterized by Dooley et al.[8]

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 reacted at reflux with 1.5 times excess concentrated HCl, added dropwise. The reaction $Na_2WO_4\cdot 2H_2O + 2\ HCl \rightarrow WO_3 + 3\ H_2O + 2\ NaCl$ will take 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 thoroughly washed with DI water followed by drying at 120°C.

Table 1. Composition and BET surface area of catalysts used.

Composition	**Surface Area (m^2/g)**
γ-Al_2O_3	170
4% La_2O_3/Al_2O_3 (Boehmite)	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

Fixed bed reactor experiments were carried out using 1.5-2.5 g of catalyst. Pure methanol was mixed with 12% H_2S/N_2 in a vaporizer held at 200C. The weight hourly space velocity of methanol (WHSV) was varied between 0.07-1.6 g/h-g cat., with a molar feed ratio of methanol to H_2S ranging from 0.3-2.2. The reactor bed temperature was varied from 360-400C and the pressure at its inlet was 1.3-1.7 bar. Catalysts were calcined in nitrogen or air prior to use at 400-500C 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 n-propanamine (n-PA) desorption using the method of Kanazirev et al.[9] 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 n-PA. Ten to 15 mg of sample was weighed out in the platinum microbalance pan and dried in 50 cm^3/min He flow via temperature programming from 50-400°C at 10°C/min with a final hold of 10 min or more. The sample was then rapidly cooled to 50°C and exposed to PA until saturated by bubbling 50 cm^3/min He through the liquid at ambient temperature. The bubbler was then bypassed and the sample was purged with pure He for 10 min at 50°C. Thermal gravimetric analysis was then performed by linearly varying the temperature from 50-550°C at 5°C/min.

RESULTS

In the following discussion, yield (MT, DMS, DME) is defined as the mole percentage of methanol fed to the reactor that reacts to form a given product. Sulfur product yield is the sum of MT and DMS yields, and the selectivity to MT or DMS is defined as the mole percentage of methanol forming sulfur products that forms MT or DMS. The affinity for a reaction 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.[10]

The catalysts studied fall into three groups based on their reactivity. The first group, consisting of La_2O_3/Al_2O_3, γ-Al_2O_3, HZSM-5 and WO_3/ZrO_2, showed significantly higher activity to sulfur products than the other catalysts. Although the catalysts in this group were not extensively investigated under identical conditions of temperature, feed ratio and yield of sulfur products, it can be concluded that the general order of specific reactivity is WO_3/ZrO_2 > La_2O_3/Al_2O_3 > γ-Al_2O_3 > HZSM-5.

La_2O_3/Al_2O_3 gave a high yield to sulfur products even at high space velocities. At a temperature of 400°C, methanol feed rates of 38-135 μmol/m^2-h (WHSV 0.39-1.40 h^{-1}), and a feed ratio (moles MeOH/moles H_2S) of 1.9-2.1, 92-97% of the methanol is converted to sulfur products with a selectivity to DMS between 89 and 96%. Looking at Table 2, it can be seen that the selectivity to DMS increases with temperature, increases with feed ratio over a range of 1.4-2.1, and decreases slightly with space velocity from 38-135 μmol/m^2-h.

Figure 1 shows how the product distribution varies with increasing conversion of methanol to sulfur products. The solid lines represent the values (at 370°C) of methanol conversion, DME yield, DMS yield, and MT yield that result from allowing reactions (3) and (4) to come to equilibrium while holding the extents of reactions (1) and (2) constant. For the sulfur product yields observed, the equilibrium lines do not vary significantly with temperature from 340-400°C so an average temperature of 370°C can be applied. The lines representing the equilibrium values of DMS and MT yields established by the disproportionation reaction do vary significantly with feed ratio; lines are drawn at feed ratios of 1.6 (the lower line for DMS and the upper line for MT) and 2.0. The equilibrium value for DMS yield at a given sulfur product yield increases with feed ratio and the value for MT yield decreases with feed ratio.

As shown in Figure 1, the conversion of methanol to DME peaks at residence times shorter than were investigated. Over the range of data collected, as the yield to sulfur products increases from 72-97%, the conversion of methanol increases only from 92-98%. The yield to DME decreases from 20-1% over the same range. The affinity for this reaction is close to zero, indicating that the reaction is close to equilibrium. From these observations it can be concluded that at longer residence times DME either directly reacts to form sulfur products, or first converts back to methanol, which subsequently reacts to form sulfur products.

At 400°C and an H_2S conversion less than 99%, the affinity of reaction (4) is close to zero, indicating that this reaction is close to equilibrium. The affinity of reaction (4) decreases with temperature from 340-400°C. The average yield to DMS (when fit by linear regression) increases from 55-89% as the sulfur product yield increases from 72-97%. The average MT yield decreases from 17 to 8% over this range.

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

Feed Ratio	**□mol/m^2-h**	**X, MeOH**	**X, H_2S**	**Y, SP**	**S, MT**	**A**
1.42± 0.66	31± 14	98± 2	78± 27	97± 3	14± 20	-0.1± 0.7
1.73± 0.13	68± 5	94± 3	82± 4	91± 5	4± 2	-2.5± 1.0
1.74± 0.04	138± 3	98± 1	99± 1	97± 1	17± 1	3.6± 1.1
1.88± 0.09	134± 6	96± 1	99± 1	95± 1	11± 2	2.3± 0.1
1.89± 0.06	84± 3	97± 1	99± 2	96± 1	8± 2	1.7*
1.91± 0.06	135± 4	96± 1	99± 1	95± 2	10± 1	3.0± 0.3
1.93± 0.08	77± 3	97± 1	99± 1	94± 2	9± 3	2.5*
2.00± 0.11	38± 2	96± 2	93± 1	90± 4	4± 2	-1.4± 1.0
2.02± 0.08	79± 3	93± 1	97± 2	91± 2	6± 3	0.3± 1.6
2.06± 0.29	359±50	93± 1	102± 4	79± 6	26± 4	
2.12± 0.11	82± 4	93± 1	96± 1	87± 3	5± 2	-0.2± 0.9

* Could not compute standard deviation; some indeterminate (infinite) values of A.

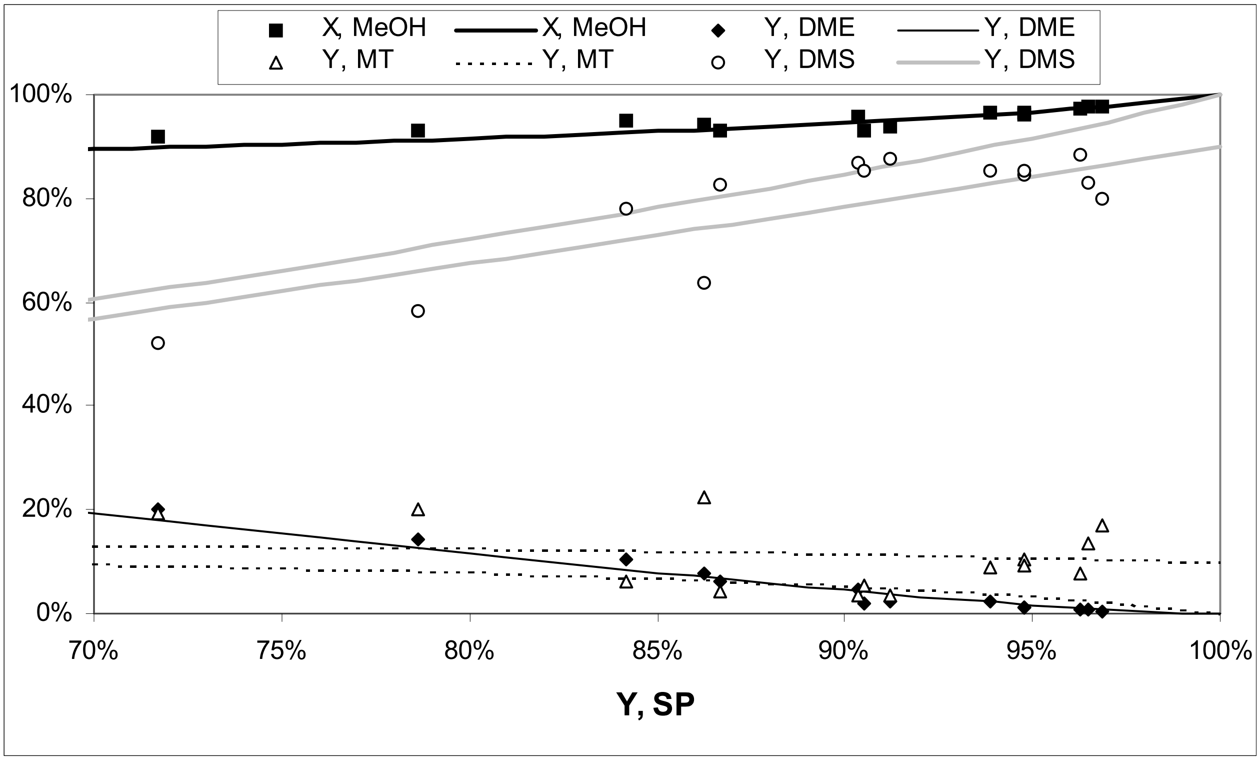

Figure 1. Yields and conversion on La_2O_3/Al_2O_3 versus yield to sulfur products at 340-400°C.

At 340°C, WO_3/ZrO_2 converts greater than 84% of the methanol to sulfur products at space velocities between 107 and 272 μmol/m^2-h (WHSV 0.27-0.68 h^{-1}) and feed ratios of 1.3-2.2. At 340°C, a space velocity of 262 μmol/m^2-hr and a feed ratio of 2.0-2.1, WO_3/ZrO_2 converts 85% of the methanol 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 40 μmol/m^2-hr, so at this temperature WO_3/ZrO_2 is more active. At 360°C, WO_3/ZrO_2 converted 1.6-2.0% of the methanol to hydrocarbons (mostly methane), so temperatures above this were not examined. As with La_2O_3/Al_2O_3, the selectivity to DMS increases by 3-5% when the temperature increases from 340 to 360°C. As shown in Table 3 this selectivity decreases with space velocity (107-262 μmol/m^2-h) and increases with feed ratio from 1.3 to 2.4.

As can be seen in Figure 2, the yields to sulfur products and DME behave in the same way at longer residence times as for La_2O_3/Al_2O_3. As the yield to sulfur products increases from 77-99%, the average DMS yield increases from 70-83% and the MT yield increases from 7-15%. When 77% of the methanol has been converted to sulfur products, the yield of DME and conversion of methanol are 17 and 94%, respectively. The DME yield decreases linearly with sulfur product yield. When 99% of the methanol has been converted to sulfur products, the DME yield is 1%. At sulfur product yields greater than 80%, the affinity for reaction (3) is less than –2, indicating that the rate of this reaction relative to the rates of reactions forming C-S bonds is lower for this catalyst than for the other catalysts that show high activity for DMS production. At 340°C, the affinity of reaction (4) is positive but close to zero for most conditions. This affinity decreases when the temperature rises to 360°C.

Table 3. Performance of WO_3/ZrO_2 at 340°C with increasing feed ratio. To convert to WHSV, divide space velocities by 401. Three runs per data point.

Feed Ratio	**□mol/m^2-hr**	**X, MeOH**	**X, H_2S**	**Y, SP**	**S, MT**	**A**
1.30± 0.08	253± 16	100 ± 1	77± 2	94± 4	26± 1	1.2± 0.1
1.35± 0.62	143± 66	100± 1	80± 35	98± 3	21± 6	1.0*
1.35± 0.10	272± 20	100± 1	82± 4	96± 1	27± 1	1.5± 0.2
1.52± 0.31	461± 94	94± 6	74± 15	77± 19	27± 5	1.1± 0.6
1.62± 0.22	262± 36	100± 1	90± 9	91± 2	21± 2	1.7± 0.8
1.66± 0.41	116± 29	100± 1	93± 23	99± 2	14± 6	1.3*
1.94± 0.07	149± 5	100± 1	96± 2	91± 1	9 ± 1	1.1± 0.5
1.99± 0.17	107± 9	99± 1	97± 2	91± 5	7 ± 2	0.8± 0.4
2.05± 0.12	262± 15	100± 1	99± 5	85± 1	14± 1	3.7*
2.18± 0.17	159± 12	99± 1	98± 1	84± 5	7 ± 1	1.0± 0.3
2.20± 0.28	108± 14	98± 1	96± 3	84± 8	3 ± 1	-1.1± 0.9
2.39± 0.16	167± 11	98± 1	98± 4	79± 3	5± 1	0.5*

The trends in the results for a γ-Al_2O_3 catalyst are 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 is achieved at a space velocity of 32 μmol/m^2-hr. At the same temperature and a similar feed ratio on La_2O_3/Al_2O_3, the conversion is 91% at a space velocity of 79 μmol/m^2-hr. At 340°C and a feed ratio of 2.3-2.4, this catalyst converted 57% of the methanol to sulfur products at a space velocity of 89 μmol/m^2-hr compared to 79% at 167 μmol/m^2-hr for WO_3/ZrO_2 at the same temperature and a similar feed ratio. Like the other two catalysts, the selectivity to DMS increases with temperature (94-99% going from 360-400C), decreases with space velocity, and increases slightly with feed ratio as shown in Table 4.

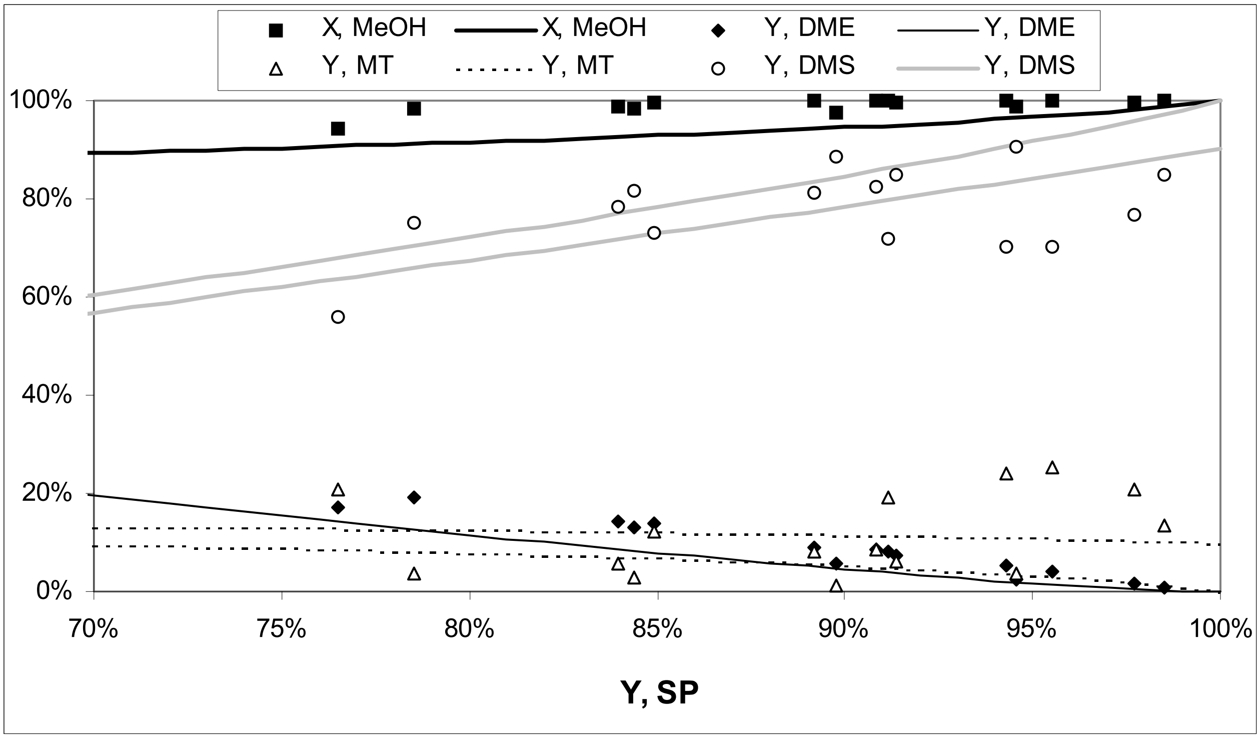

Figure 2. Yields and conversion on WO_3/ZrO_2 versus yield to sulfur products at 340°C. The equilibrium lines have the same meaning as in Figure 3.1 but are drawn at 340°C.

Trends in methanol conversions and DME yields vs. sulfur product yields for γ-Al_2O_3 are also similar to those of the previous two catalysts, as seen in Figures 3-4. When 57% of the methanol has been converted to sulfur products, the DME yield is 32% and the methanol conversion is 89%. As the yield to sulfur products increases to 94%, the yield of DME decreases linearly to 2% and the conversion of methanol increases to 96%. Under all conditions investigated, the affinity is negative for the reaction to DME, although it is close to equilibrium ($-1 < A < 0$). For all conditions investigated, affinity is negative for reaction (3), although it is close to equilibrium ($-1 < A < 0$). For all conditions investigated, the affinity for reaction (4) is negative, indicating that this reaction produces MT from DMS near the reactor exit. Figure 4 shows that DMS yield increases while the MT yield remains relatively constant as methanol conversion increases from 89-97%. As the sulfur product yield increases from 57-94%, the average DMS yield increases from 54-89%, but the MT yield only increases from 3-5%.

HZSM-5 was the least active of the four catalysts in the first group. Compared to γ-Al_2O_3 at 400°C and a feed ratio of 1.7-1.8, 77% of the methanol is converted to sulfur products over HZSM-5 at a WHSV of 0.37 h^{-1}, compared to 94% for γ-Al_2O_3 at the same conditions. However, HZSM-5 was the least selective catalyst to MT, with this selectivity being less than 5% at 400°C for most conditions. Just as for the other catalysts in this group, the selectivity to DMS increases with temperature (88-96% going from 340-400C) and decreases with space velocity (94-93% going from 30-50 $\mu mol/m^2$-h). Unlike most of the other catalysts examined, the selectivity to DMS decreases slightly (3-4%) with increasing feed ratio (1.8-2.0).

Table 4. Performance of γ-Al_2O_3 at 400°C with increasing feed ratio. Divide space velocity by 184 to give WHSV. Three runs per data point.

Feed Ratio	**μmol/m^2-hr**	**X, MeOH**	**X, H_2S**	**Y, SP**	**S, MT**	**A**
1.52± 0.44	57± 17	96± 1	81± 15	94± 2	13± 12	-0.2± 0.8
1.75± 0.10	65± 4	97± 1	90± 1	94± 3	9± 3	-0.1± 0.7
1.87± 0.10	34± 2	96± 2	89± 2	92± 5	3± 1	-2.7± 1.2
1.87± 0.02	46± 1	95± 2	89± 1	92± 1	4± 1	-2.0± 0.6
2.07± 0.06	32± 1	94± 1	90± 1	86± 2	1± 1	-4.4± 0.5
2.39± 0.17	40± 3	92± 1	94± 2	78± 3	1± 1	-4.3± 0.6

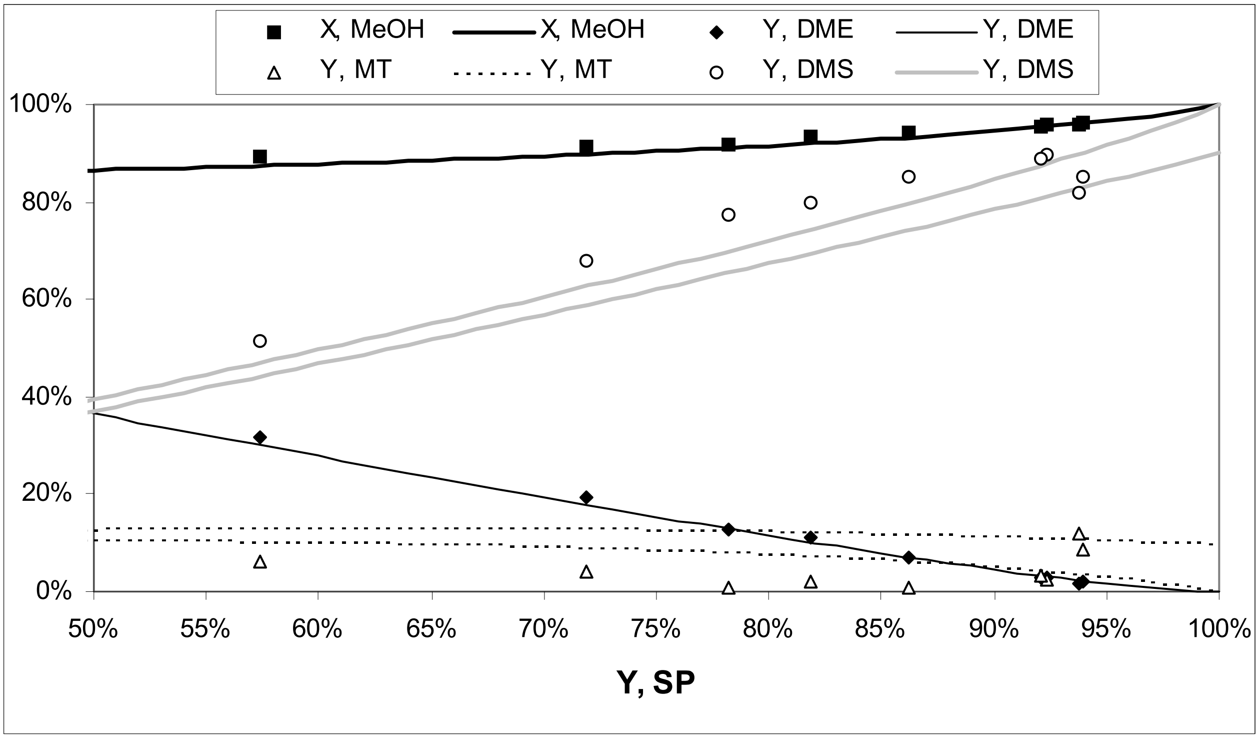

Figure 3. Yields and conversion on γ-Al_2O_3 versus yield to sulfur products at 340-400°C. The equilibrium lines have the same meaning as in Figure 3.1.

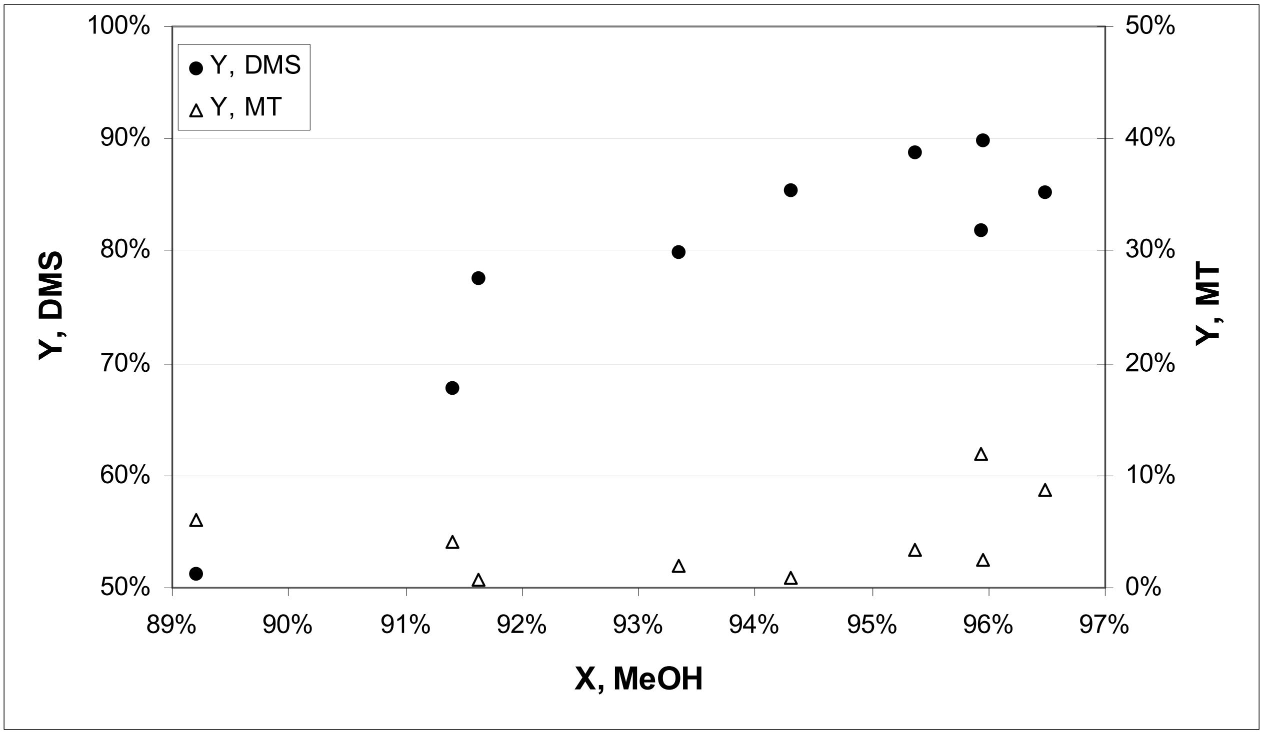

Figure 4. Yield to DMS and MT versus methanol conversion on γ-Al_2O_3.

As the yield to sulfur products increases from 51 to 77%, the DME yield decreases from 21 to 14% and the methanol conversion increases from 72 to 91% (Figure 5). It appears that at lower sulfur product yield (50-65%) the yield of DME is constant and the affinity for its production is positive. At higher yields, the yield to DME decreases and closely follows the equilibrium value with an affinity close to zero. Like the γ-Al_2O_3 catalyst, the affinity for MT disproportionation is negative, so MT is produced from DMS near the reactor exit. But Figure 6 shows clearly that the yield to DMS increases and the yield to MT decreases or remains constant as methanol conversion increases from 70-90%. As the sulfur product yield increases from 51-74%, the average DMS yield increases from 44-71%, and the average MT yield decreases from 7 to 3%.

The second group of catalysts consists of WO_3/Al_2O_3, MoO_3/SiO_2, SAPO-18 and AlPO-18. These are less active than those of the first group for the sulfidation of methanol, but are more selective to MT.

WO_3/Al_2O_3 is the most selective catalyst to MT that was examined; reaction results are shown in Figures 7 and 8. Over a wide range of conditions, with feed ratios between 0.3 and 0.7, the selectivity of MT is greater than 80%. Temperatures from 340-400°C and space velocities from 14-59 μmol/m^2-h (WHSV 0.07-0.30) were investigated. Under all conditions, increasing the temperature and feed ratio as well as decreasing the space velocity decreased the MT selectivity as shown in Table 5; this is also evident from the large positive affinity values for MT disproportionation (3-4). The highest selectivity to MT of 93% was obtained at 340°C, a feed ratio of 0.33 and a space velocity of 74 μmol/m^2-hr. At 400°C, a feed ratio of 0.31 and a space velocity of 26 μmol/m^2-h, 94% of the methanol is converted to sulfur products with 91% of this amount being MT.

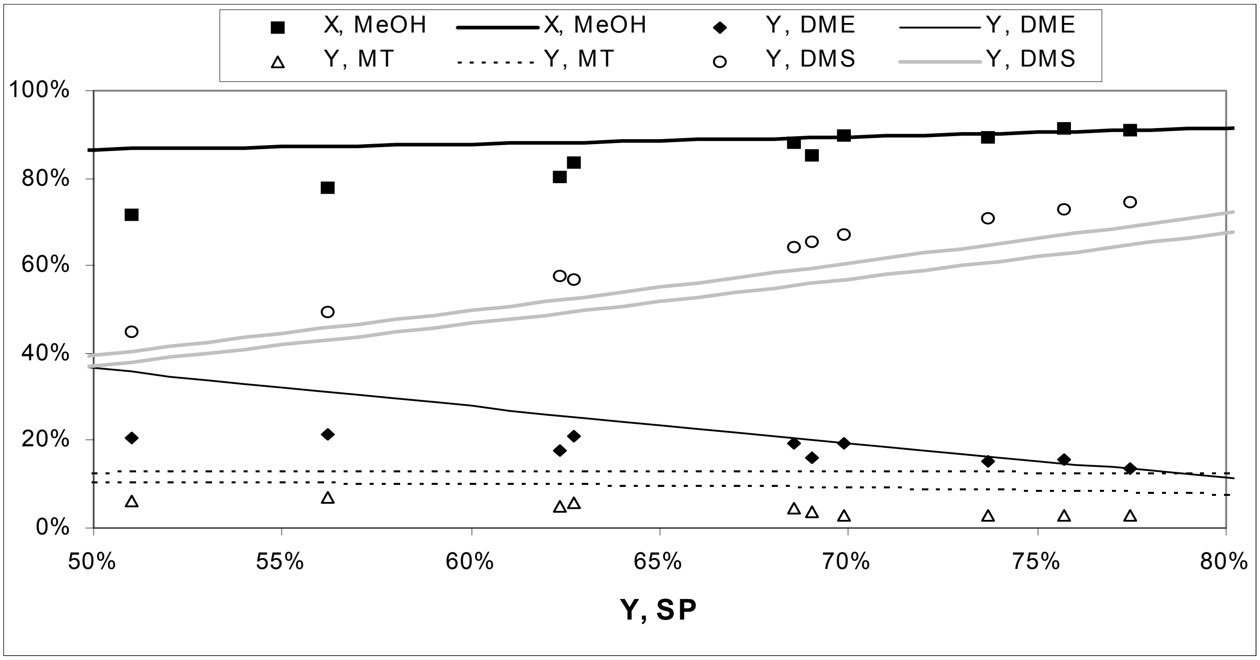

Figure 5. Yields and conversion on HZSM-5 versus yield to sulfur products at 340-400°C. The equilibrium lines have the same meaning as in Figure 3.1.

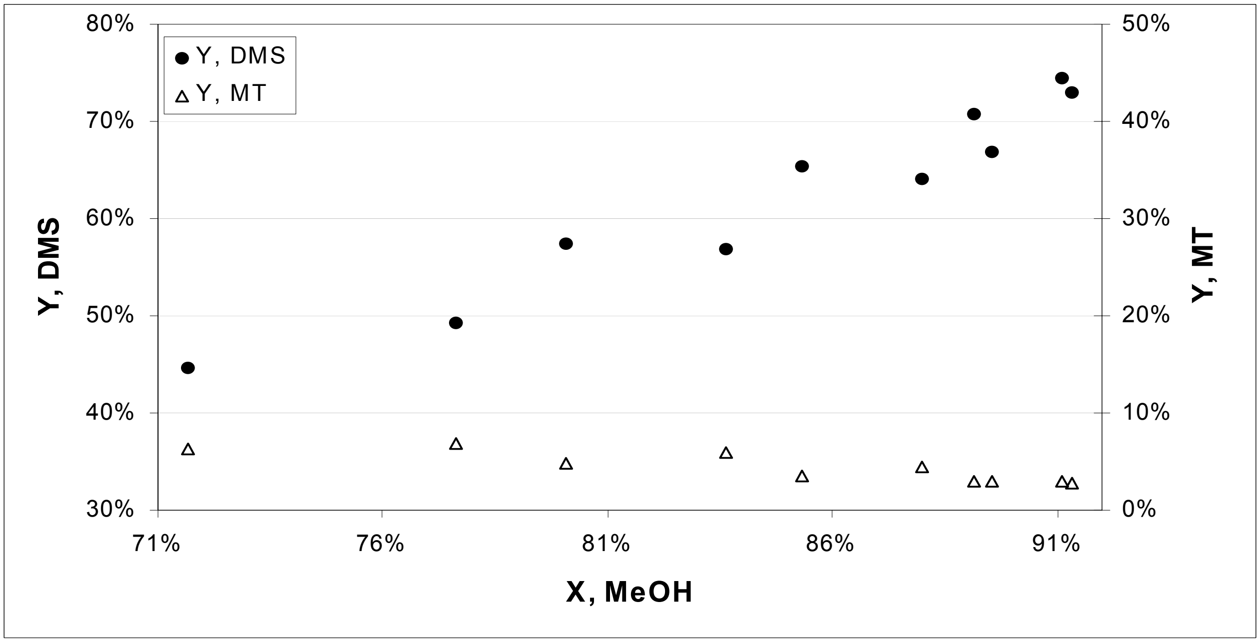

Figure 6. Yield to DMS and MT versus methanol conversion on HZSM-5.

At sulfur product yields less than 90%, the affinity for DME production is positive; at higher sulfur product yields the DME and methanol are close to equilibrium. As the sulfur product yield increases from 40 to 96%, the DME yield decreases from 17 to 1% and the methanol conversion increases from 55 to 99%. Figure 8 shows that both DMS and MT yields increase with methanol conversion increasing from 50-100%. As the sulfur product yield increases from 40-96%, the average MT yield increases from 36-85%, and the average DMS yield increases from 3-11%.

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

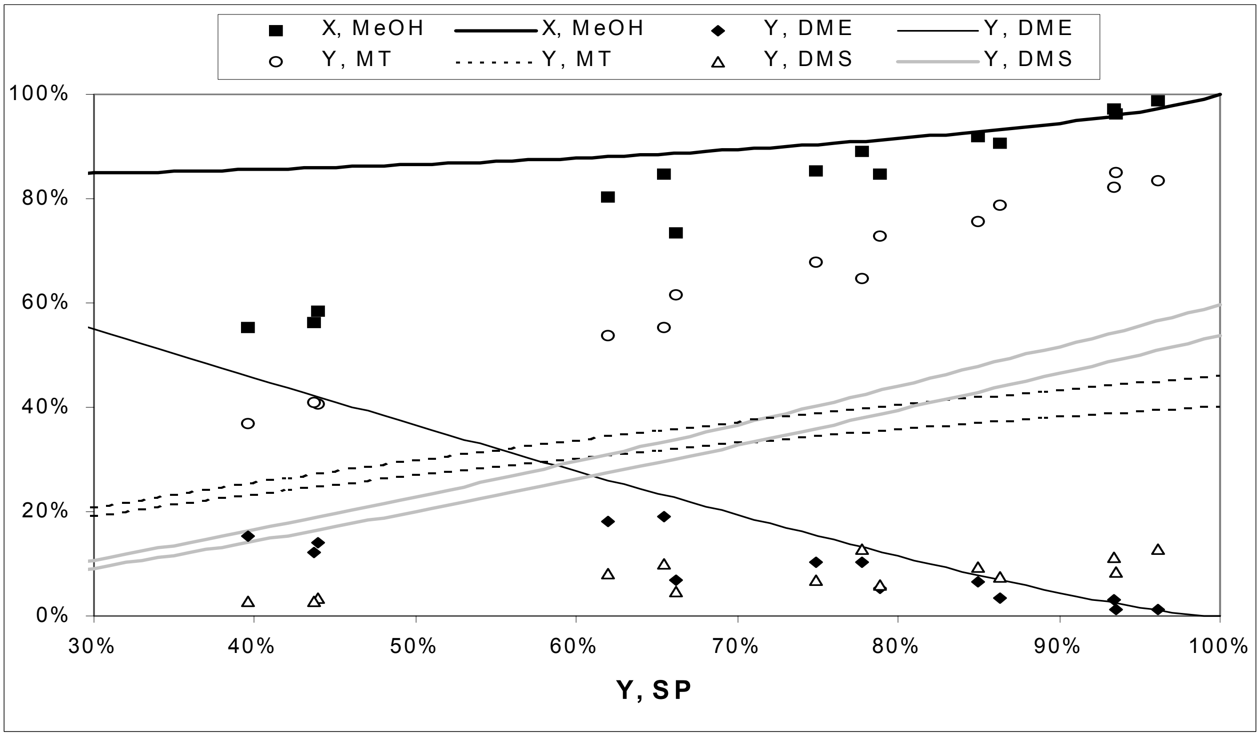

Figure 7. Yields and conversion on WO_3/Al_2O_3 versus yield to sulfur products at 340-400°C. Equilibrium lines have same meaning as in Figure 3.1 but are drawn at feed ratios of 0.3 (lower curve, DMS and upper curve, MT) and 0.4.

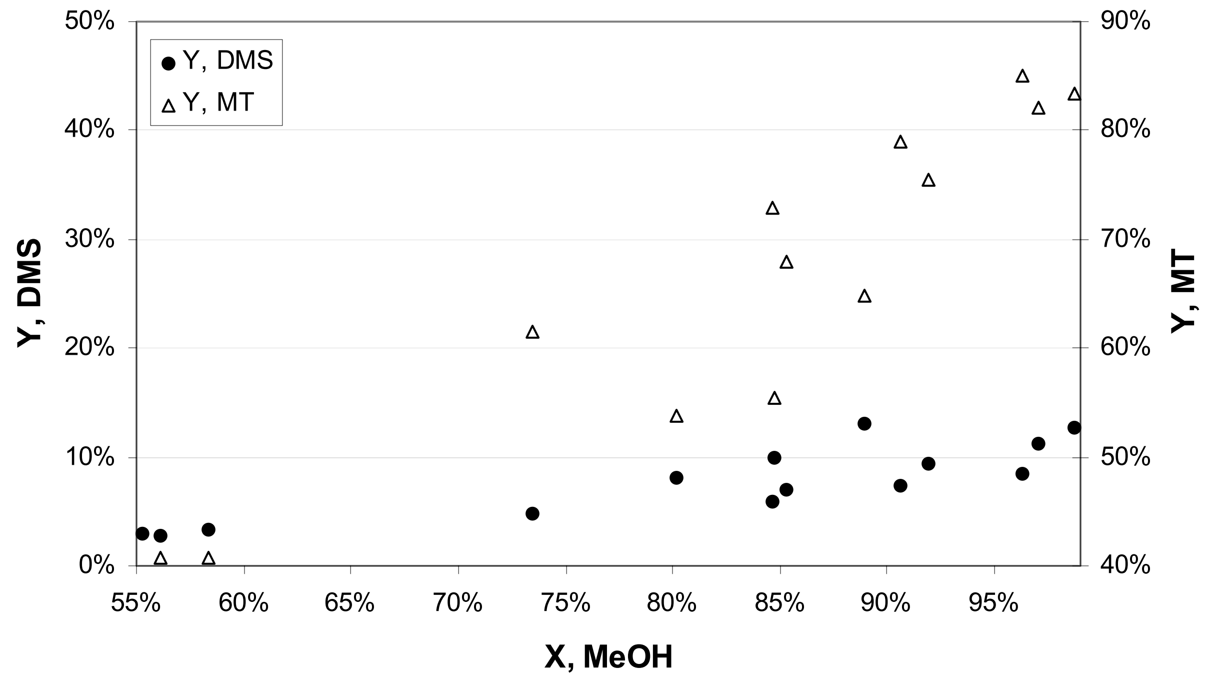

Figure 8. Yield to DMS and MT versus methanol conversion on WO_3/Al_2O_3.

SAPO-18 and AlPO-18 were chosen to match the pore size of the catalyst (3.8 Å for these materials) to the molecular diameter of DMS (4.1 Å) in an attempt to achieve shape selectivity to this product. Both catalysts make mostly DME. At 360-400°C, the 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 (WHSV 0.48-0.58). When the sulfur product yield was 6%, the MT selectivity was 63%. This selectivity decreased to 11% as the yield increased to 43%. 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 catalyst 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 a temperature of 400°C, a feed ratio of 2.9 and a space velocity of 16 μmol/m^2-h (WHSV 0.24). The selectivity to MT was 47% when the sulfur product yield was 10% and dropped to 17% when the yield was 32%. Similar activity to DME was observed as for SAPO-18.

Less than 1% of the methanol was converted to sulfur products by TiO_2/SiO_2, making it the least active catalyst among those studied. Reaction conditions were a temperature of 400°C, a feed ratio of 2.5 and a space velocity of 21 μmol/m^2-h (WHSV 0.26). Some DME was produced, but it could not be accurately quantified due to the close proximity of the large methanol peak.

Table 5. Performance of WO_3/Al_2O_3 with increasing temperature from 340-400°C. Space velocity for first four entries is 36-44 μmol/m^2-h, for second four it is 26-28 μmol/m^2-h and for last four it is 14-16 μmol/m^2-h. To convert to WHSV, divide space velocity by 194. Three runs per data point.

Temp. (°C)	**Feed Ratio**	**X, MeOH**	**X, H_2S**	**Y, SP**	**S, MT**	**A**
340	0.70 ± 0.09	58± 5	29± 1	44± 4	93± 1	3.5± 0.1
360	0.61 ± 0.14	80± 9	35± 3	62± 10	87± 1	3.1± 0.1
380	0.74 ± 0.04	85± 3	45± 2	65± 1	85± 1	3.3± 0.1
400	0.66 ± 0.01	89± 1	47± 1	78± 1	83± 1	3.2± 0.1
340	0.33 ± 0.04	74± 5	21± 1	66± 5	93± 1	3.2± 0.1
360	0.32 ± 0.01	85± 2	25± 1	79± 2	92± 1	3.2± 0.1
380	0.34 ± 0.06	91± 5	28± 3	86± 6	91± 1	3.2± 0.1
400	0.31 ± 0.01	96± 2	28± 1	94± 2	91± 1	3.2± 0.1
340	0.47 ± 0.05	85± 5	34± 1	75± 5	91± 1	3.5± 0.1
360	0.46 ± 0.07	92± 5	37± 3	85± 7	89± 1	3.4± 0.1
380	0.42 ± 0.08	97± 2	37± 6	93± 3	88± 1	3.2± 0.1
400	0.43 ± 0.04	99± 1	38± 3	96± 2	87± 1	3.2± 0.1

To measure deactivation catalysts were kept on-stream for two days, 8-10 hours a day, at typical operating conditions. After this, catalysts were regenerated overnight in 20-50 mL/min of air (STP) at temperatures of 400°C for the mixed metal oxides and 500°C for HZSM-5 (higher thermal stability than some of the mixed metal oxides). La_2O_3/Al_2O_3 and γ-Al_2O_3 did not show any sign of deactivation over the two-day period. HZSM-5 and WO_3/Al_2O_3 deactivated by about 8% DMS/MT yield but were completely regenerated. WO_3/ZrO_2 deactivated by 10% DMS yield and 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 in the first place.

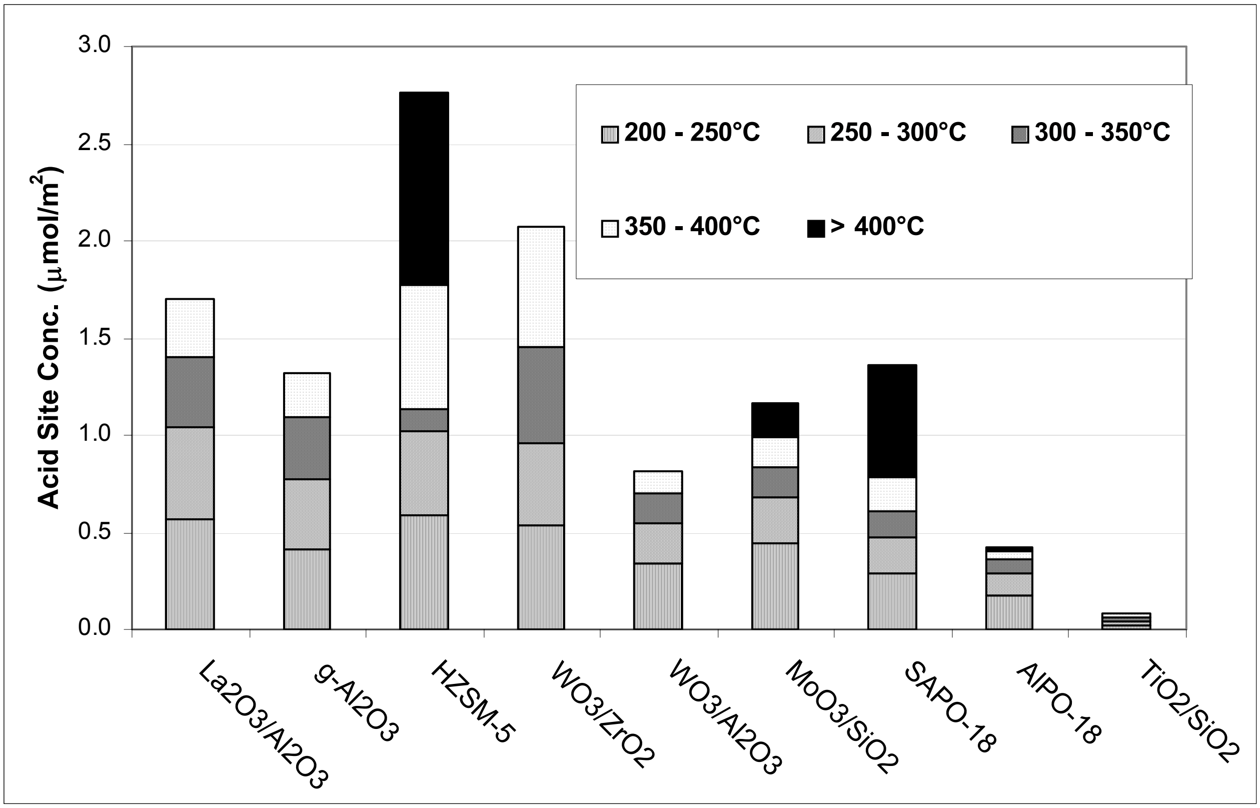

Figure 9. Concentration of acid sites determined by the desorption of propanamine in different temperature ranges.

Data from the 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 by assuming that desorption of 1-propanamine or its Hoffmann elimination products propene and ammonia occurs on stronger sites at higher temperatures.[9] It should be noted that this method does not distinguish between LCs and PCs, since 1-propanamine can adsorb on both types of sites. All of the samples that were analyzed showed a low temperature desorption peak centered between 50 and 150°C, while HZSM-5, SAPO-18 and WO_3/ZrO_2 showed other peaks centered 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. All catalysts had 2-6 μmol/m^2 of weak sites characterized by desorption below 200°C. TiO_2/SiO_2 showed a large number of sites at below 150°C, but it was inactive in the presence of MeOH and H_2S. Furthermore, the catalysts showing low activity had a large number of sites between 150 and 200°C, so weak sites characterized by propanamine desorption below 200°C are probably not active for any of the reactions studied here.

The number of acid sites desorbing 1-propanamine or its Hoffmann elimination products at >200°C is shown in Figure 9 for each catalyst. Comparing 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 sites that desorb between 200 and 400°C, the concentration being 1-2 □mol/m^2. Roughly 0.5 mmol/m^2 of sites are characteristic of 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. HZSM-5 has a desorption peak centered in this region and it was found by Kanazirev et al.[9] that this peak is due to the desorption of one molecule of propanamine from an acid site where two were initially adsorbed. Because there is no Hoffmann elimination associated with this desorption, the concentration of these sites probably does not correlate directly to reactivity.

Among the four active (to DMS) catalysts, the number of sites in the 300-350°C regime vary from 0.3 to 0.5 μmol/m^2, decreasing in the order WO_3/ZrO_2 > La_2O_3/Al_2O_3 > γ-Al_2O_3 > HZSM-5. This is the same order as was found for the activity of these catalysts for sulfur products, indicating that sites desorbing in this range are probably 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 > γ-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.

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 0.4-1.0 μmol/m^2. The number of sites desorbing between 200 and 300°C ranges from 0.3-0.7 μmol/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 300-350°C ranges from 0.1-0.2 μmol/m^2, decreasing in the order MoO_3/SiO_2 ~ 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 350-400°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 μmol/m^2 of propanamine respectively.

The TiO_2/SiO_2 catalyst desorbed very little 1-propanamine between 200 and 400°C, with 0.1 μmol/m^2 total sites distributed evenly among the temperature ranges. Nothing was retained at above 400°C.

DISCUSSION

The fixed bed reactor experiments show that La_2O_3/Al_2O_3, γ-Al_2O_3, WO_3/ZrO_2, and HZSM-5 are active and selective for DMS. WO_3/ZrO_2 was the most active of these at 340°C, although it was not suitable for DMS production at higher temperatures due to a significant conversion of methanol to methane. At 360°C on this catalyst, 1.6-2.0% of the methanol was converted to methane compared to less than 1% at 340°C. At 400°C, the activities of the other three catalysts decreased in the order La_2O_3/Al_2O_3 > γ-Al_2O_3 > HZSM-5 and the yield to hydrocarbons was less than 1%. Conditions could be found for all of these catalysts, except for HZSM-5 (340°C for WO_3/ZrO_2, 400°C for the other two), at which more than 90% of the methanol was converted to sulfur products at a WHSV greater than 0.35 h^{-1}. At these conditions, the selectivity to MT was less than 10% for molar feed ratios of methanol to H_2S greater than 1.8. On HZSM-5, greater than 75% sulfur product yield was achieved along with an MT selectivity less than 5% at conditions similar to those of the other catalysts.

On these catalysts, it was observed that MT yield decreased slightly or remained constant with increased contact time, while the DMS yield increased. The yields of both sulfur products were close to the equilibrium values calculated at a given total sulfur product yield (see section 3.1 for calculation details). These observations are not consistent with a purely serial mechanism ($H_2S \rightarrow MT \rightarrow DMS$), but instead suggest that MT disproportionation is fast and close to equilibrium. Since the disproportionation reaction is fast, MT in the product stream can be separated and recycled to the feed to be converted to DMS. It was also observed that MT selectivity decreases with increased feed ratio.

For all four of these catalysts, the DME yield decreased with contact time, with DME decomposing predominantly to sulfur products. It was observed that for La_2O_3/Al_2O_3 and γ-Al_2O_3, DME and methanol are close to their equilibrium concentrations at a given yield of sulfur products. For WO_3/ZrO_2, the DME yield is slightly greater than the calculated equilibrium value (see section 3.1 for details of this calculation); for HZSM-5, it is slightly less. This indicates that the reaction forming DME from methanol is also fast and close to equilibrium. Thus, DME in the product stream 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 indicates that sites desorbing in the range of 300-350°C are responsible for most of the activity to sulfur products. The number of sites in this range for these catalysts decreases in the same order as the activity ($WO_3/ZrO_2 > La_2O_3/Al_2O_3 > \gamma$-$Al_2O_3 >$ HZSM-5). HZSM-5 was the only catalyst of this group to retain the reaction products of 1-propanamine above 400°C.

Fixed bed reactor experiments showed WO_3/Al_2O_3 to be active and selective to MT, with DMS selectivity less than 15%. Conversions of methanol to sulfur products greater than 90% could be achieved only at a low WHSV of 0.14 h^{-1}, so WO_3/Al_2O_3 is less active than the four catalysts in the first group. Yields to MT and DMS are far from their calculated equilibrium values, indicating that the disproportionation reaction is slower on this catalyst. The DME yield is slightly below its calculated equilibrium value at a given sulfur product yield and decreases with contact time, indicating the reaction forming DME from methanol is fast and close to equilibrium. Therefore, DME can be recycled, and it may also be possible to recycle DMS for conversion back to MT via the disproportionation reaction.

For all of the catalysts discussed above, the selectivity to sulfur products does not decrease as the partial pressure of methanol decreases by orders 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 found to be unsuitable for either MT or DMS production. Mo_3/SiO_2 had low selectivity to sulfur products and produced a large amount of carbonyl sulfide. SAPO-18 and AlPO-18 had low activity and TiO_2/SiO_2 had almost no activity. For these catalysts and WO_3/Al_2O_3, it was also found that acid sites desorbing reaction products of 1-propanamine in the range 300-350°C were probably responsible for the formation of most sulfur products.

Based on experimental results in this and previous work, along with the catalytic chemistry associated with metal oxides, a mechanistic pathway emerged that explained the activity of the catalyst in sulfidation of methanol and the distribution of products (Figure 10). By examining experimental results for this reaction from the relevant literature, it can be seen that the activity is highest for catalysts with LCs of moderate strength (Q_{CO} of 30-40 kJ/mol)[2]. Alumina falls in this range and the activity sharply decreases when the cation is replaced with a neighboring element on the periodic table (Mg and Si). It is also apparent that basic catalysts are selective to MT while more acidic catalysts favor DMS.

In order to understand the mechanism leading to this behavior, details about the 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 H_2O in the gas phase. It is expected that methanol and water have roughly the same adsorption energy on an LC/BC pair since the O-H bonds that are broken in the adsorption of both molecules have similar acidity. Water has a higher adsorption energy on alumina than does H_2S. At low conversion, methanol should be the most abundant surface species, and at high conversion, water.

Ab-initio calculations were performed in this work using Gaussian 03 [11] to determine the difference in binding energies of hydroxyl and bisulfide species with an LC. Clusters consisted of a cation (Na^+, Mg^{2+}, Al^{3+}, and Si^{4+}) coordinated to O^{2-} and OH^- ligands to balance the charge. 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 on 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. It therefore seems that on alumina, H_2S coverage should be significantly below a monolayer, and this coverage should increase with the basicity of the catalyst.

The surface acidity/basicity determines the surface bond strengths. On 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 protons and methyl groups.[12] As the surface becomes basic, this trend reverses; the binding of oxygen and sulfur with the lattice weakens and their binding to protons and methyl groups strengthens. Due to these effects, the reactivity of surface protons and methyl groups initially increases with acidity and decreases with basicity; the reactivity of adsorbed sulfur and oxygen follows the opposite trend.

Ab-initio calculations using Gaussian 03 [11] were performed in this work on 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. It was found that the bond energy decreased in the order O-H (1610-1640 kJ/mol) > S-H (1470-1500 kJ/mol) > C-O (1160-1180 kJ/mol) > C-S (1040-1070 kJ/mol).

Insight into the effects of surface acidity on the mechanistic pathway can be gained by taking into account the trends in activity and selectivity in the experimental data. The rate determining step of each path will have a minimum activation barrier at a certain level of surface acid strength. On alumina-based catalysts, the activity initially increases with acid strength, but eventually decreases for more acidic catalysts such as alumino-silica and PO_4^{3-}/SiO_2.[2] The selectivity of DMS (vs. MT) is found to be highest on alumino-silica (91%

selectivity), being lower for less acidic catalysts such as alumina. The activation barrier heights of paths leading to both DMS and MT appear to be low at acid strengths close to alumina, however, the minimum barrier height of the second methyl addition occurs at higher acid strength - 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.

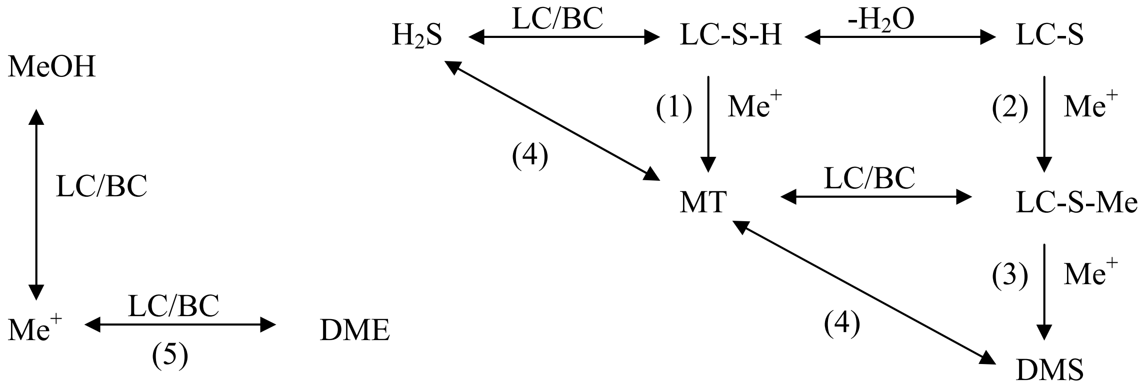

Figure 10. Diagram showing the relations between paths in the overall mechanism.

CONCLUSIONS

The conclusions that can be drawn from this work are the following:

- WO_3/ZrO_2, La_2O_3/Al_2O_3, γ-Al_2O_3, and HZSM-5 are suitable catalysts for the production of DMS from methanol and H_2S while WO_3/Al_2O_3 is suitable for the production of MT.
- The reaction that produces DME from methanol is fast and close to equilibrium on most catalysts. Most of the methanol is converted to DME at short contact times, and at longer contact times the DME converts to sulfur products.
- For good DMS catalysts, the DMS yield increases with conversion while the MT yield remains relatively constant. This is not consistent with a purely serial mechanism and indicates that the disproportionation reaction is fast and close to equilibrium on these catalysts.
- The selectivity to sulfur products does not decrease significantly as the methanol partial pressure decreases, indicating that the reaction is close to zero order in methanol.
- The selectivity to MT decreases with increasing feed ratio, temperature, and contact time.
- Acid sites desorbing n-propanamine between 300-350°C are the most active sites for the sulfidation reactions.
- The transfer of the second methyl group to an adsorbed sulfur atom to form DMS is more difficult than transferring the first methyl group to form MT, and requires stronger acid sites.

REFERENCES

(1) Mashkin, V. Y.; Kudenkov, V. M.; Mashkina, A. V. *Ind. Eng. Chem. Res.* **1995,** 34, 2964-2970.

(2) Mashkina, A. V.; Paukshtis, E. A.; Yakovleva, V. N. *React. Kinet. Catal. Lett.* **1988,** 29, (3), 514-520.

(3) Mashkina, A. V.; Yakovleva, V. N.; Khairulina, L. N. *React. Kinet. Catal. Lett.* **1991,** 43, (2), 405-411.

(4) Mashkina, A. V.; Yakovleva, V. N. *React. Kinet. Catal. Lett.* **1991,** 32, (3), 636-641.

(5) Ziolek, M.; Nowak, I.; Decyk, P.; Kujawa, J. *Stud. Surf. Sci. Catal.* **1998,** 117, 509-516.

(6) Ziolek, M.; Kujawa, J.; Saur, O.; Lavalley, J. C. *J. Phys. Chem.* **1993,** 97, 9761-9766.

(7) Chen, J.; Wright, P. A.; Thomas, J. M.; Natarajan, S.; Marchese, L.; Bradley, S. M.; Sankar, G.; Catlow, C. R. A.; Gai-Boyes, P. L.; Townsend, R. P.; Lok, C. M. *J. Phys. Chem.* **1994,** 98, 10216-10224.

(8) Dooley, K. M.; Price, G. L.; Kanazirev, V. I.; Hart, V. I. *Catal. Today* **1996,** 31, 305-315.

(9) Kanazirev, V. I.; Dooley, K. M.; Price, G. L. *J. Catal.* **1994,** 146, 228-236.

(10) Boudart, M. *Ind. Eng. Chem. Fundam.* **1986,** 25, 70-75.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Jr., J. A. M.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, C.02; Gaussian, Inc.: Wallingford Ct, 2004.

(12) Henrich, V. E.; Cox, P. A., The Surface Science of Metal Oxides. In ed.; 'Ed.'^'Eds.' Cambridge University Press: Cambridge, 1994; 'Vol.' p^pp 284-285.