Catalysis Letters Vol. 100, Nos. 3–4, April 2005 (© 2005)
DOI: 10.1007/s10562-004-3441-x

Complete reduction of 2-chloroethylethylsulfide by hydrodesulfurization using mo-doped mesoporous substrates

Adam C. Sorensen, and Christopher C. Landry*

Department of Chemistry, University of Vermont, Cook Physical Science Building, 82 University Place, Burlington, VT 05405

Received 29 September 2004; accepted 18 December 2004

Bis(2-chloroethyl)sulfide, commonly known as mustard gas, is a highly toxic compound that acts as a vesicant, primarily by hydrolysis to produce HCl [1]. Prior to the 1960's, this compound was synthesized and stored at various locations throughout this country and the world [2–4]. The inherent danger in storing this chemical has led to efforts to degrade it by various means. Stockpiles of mustard gas are currently destroyed by incineration, which, even when complete, can release environmentally unfavorable compounds such as sulfoxides, sulfones, carbon monoxide, and carbon dioxide into the atmosphere. Most other chemically-based techniques used to react bis(2-chloroethyl)sulfide have relied on oxidative pathways, whether using solution- or solid-based approaches [5–7]. These reactions have the same environmental problems as incineration. In addition, a highly oxidizing agent can often lead to bis(2-chloroethyl)sulfone, which is nearly as toxic as mustard gas itself [8].

KEY WORDS: hydrodesulfurization; Mo-doped substrates; mustard gas.

1. Discussion

In contrast to incineration, hydrodesulfurization (HDS) is a reductive process that leads to reduced hydrocarbons and H_2S. We have recently completed a comparison of several types of substrates for the hydrodesulfuration of thiophene, which has been used in the past as a model compound for bis(2-chloroethyl)sulfide [9]. In this study, the mesoporous silicas MCM-41 [10,11], MCM-48 [10,11] and APMS-30 [12–14] (Acid-Prepared Mesoporous Spheres, 30 Å pores) were doped with Mo by several methods, and a flowing stream of H_2-saturated thiophene was passed over these solids at advanced temperatures (300–400 °C). Of these substrates, Mo-doped APMS-30 showed the highest conversion of thiophene. In contrast to the other mesoporous substrates, which required post-synthetic doping methods that resulted in decreased surface areas and pore volumes, Mo-APMS-30 could be prepared by an in situ process in which ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}$, was added to the APMS-30 reaction mixture. The HDS catalyst could therefore be prepared in a one-step process that was complete in less than 2 h. By replacing the standard furnace calcination of the product with a calcination procedure that utilized a conventional microwave oven, the completed catalyst could be prepared in less than a day [15]. The results reported here illustrate the use of Mo-APMS-30 to catalyze the reduction of 2-chloroethylethylsulfide (CEES) by HDS. CEES has a molecular structure that is more similar to bis(2-chloroethyl)sulfide than thiophene, and is used most frequently to safely model bis(2-chloroethyl)sulfide reactivity in laboratory settings [16–18]. We also compare the reactivity of "CoMo" doped substrates and Mo-only substrates, since doping of Co has been shown to enhance HDS reactivity [19,20]. These results are the first illustration of CEES decomposition by this method.

Mo-doped APMS-30 was prepared as previously described. In this method, ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}$, was added directly to the acidic aqueous solution in which APMS-30 was synthesized. To prepare substrates containing both Co and Mo, $Co(NO_3)_2 \cdot 6H_2O$ was added to the same solution. In acidic solutions, Mo forms anionic clusters that are easily incorporated into the cationic silica framework as it polymerizes from the $Si(OEt)_4$ source through electrostatic interactions. However, Co forms hydrated cations at the same pH and is incorporated into the silica only in small amounts. The substrates therefore contain mostly Mo with a small amount of Co. The Co:Mo molar ratio is in the same range as that used in other studies [20–22]. Elemental analysis was used to determine that the substrates used in this study contained 2, 5 and 10 wt% Mo (abbreviated 2-Mo-30, 5-Mo-30, and 10-Mo-30) and 2 wt% Mo/0.2 wt% Co (2-CoMo-30), 5 wt% Mo/0.2 wt% Co (5-CoMo-30), and 10 wt% Mo/0.2 wt% Co (10-CoMo-30). Following synthesis, the substrates were calcined in air to remove the surfactant template and produce the porous solid. Powder X-ray diffraction (XRD) showed that none of the samples contained crystalline Mo or Co species that were observable by this technique. N_2 physisorption showed that the samples had average pore diam-

---

* To whom correspondence should be addressed.
E-mail: christopher.landry@uvm.edu.

eters, surface areas, and pore volumes of 29 Å, 1050 m^2/g, and 0.59 cm^3/g, respectively. After synthesis and initial characterization, the samples were used to react with CEES by HDS. For comparison, a commercial HDS catalyst (Co/Mo dispersed on Al_2O_3, Strem Chemicals; 9 wt% Mo, 2 wt% Co) was also tested. The solid was pressed into a pellet and broken into pieces approximately 2 mm in diameter; 0.5 g of these pieces were then placed inside a quartz tube. Mustard gas and CEES are oily liquids with low vapor pressures (mustard gas, 0.11 mm Hg @ 25 °C; CEES, 44 mm Hg @ 73 °C) [23]. Consequently, CEES was heated slightly (38 °C) in a bubbler to increase its vapor pressure. In addition, a rapid flow rate (300 mL/min of H_2) was used to produce a saturated stream, which was passed through the quartz tube. During reaction, the quartz tube was heated to 200, 250 or 300 °C. Degradation products were determined by GC–MS.

Figure 1 shows the total conversion of CEES as a function of time for samples with 2 and 5 wt% Mo, with and without Co. All samples showed reactivity toward CEES under these conditions, ultimately reaching conversions of 60% or greater. In addition, all samples showed a significant drop in activity within the first 30 min, followed by recovery to similar activity levels. This is due to the formation of sulfided Mo species within the substrate [24]. A comparison of the types of products obtained at the shortest exposure times to those obtained at longer reaction times is consistent with this process. At the shortest time, the oxygen-containing products acetaldehyde and chloroacetaldehyde were observed in addition to reduction products of CEES, while at longer exposure times (after the drop in activity) these products were not observed. Since the only oxygen source under these conditions was the substrate itself, the formation of aldehydes must result in transfer of sulfur to the substrate. One explanation for the existence of aldehydes in a reducing environment may be the high flow rate, which carried the products into the detection system before reduction could occur. Although the active Mo species after sulfidation has been shown to be MoS_2 [25,26], no crystalline Mo species were observed by powder X-ray diffraction in the substrates after HDS. Elemental analysis of the substrates after HDS showed Mo:S ratios less than 2, indicating that sulfidation was incomplete. Thus, it is likely that the Mo was either partially sulfided and amorphous or existed as a combination of MoO_3 (fully oxidized, after calcination in air) and MoS_2, with crystallite sizes that were too small to be observed by powder XRD. Finally, it is interesting to note that the samples containing 2 wt% Mo required at least twice as much time to reach peak activity as the samples containing 5 wt% Mo. This could be due to the greater accessibility to Mo in substrates with higher concentrations.

Further experiments were performed in order to examine the catalytic abilities of samples that had been "pre-sulfided" prior to HDS. Other researchers have found that pre-sulfiding the Mo catalyst prior to HDS can lead to a more active catalyst than allowing it to gain sulfur *in situ* [27–29]. To this end, the substrates were exposed to an H_2S/H_2 mixture (25% H_2S in H_2) for 1 h at 200 °C in the quartz reaction tube just prior to HDS. After this time, H_2S was switched-off and HDS conditions identical to those described above were applied, without removal of the substrates from the tube. The resulting CEES conversions with respect to time are shown in figure 2. All substrates showed very high activity at all times. Under these conditions, 2-CoMo-30 was significantly more active than 2-Mo-30. The activity of 5-Mo-30 was sufficiently high that the addition of Co did not make a

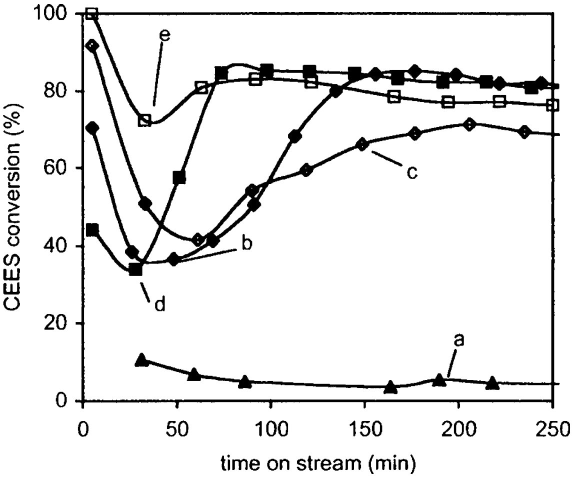


Figure 1. CEES conversions at 300 °C as a function of time. Samples were not sulfided prior to use. (a) Undoped APMS-30, for comparison, closed triangles; (b) 2-Mo-30, closed diamonds; (c) 2-CoMo-30, open diamonds; (d) 5-Mo-30, closed squares; (e) 5-CoMo-30, open squares.

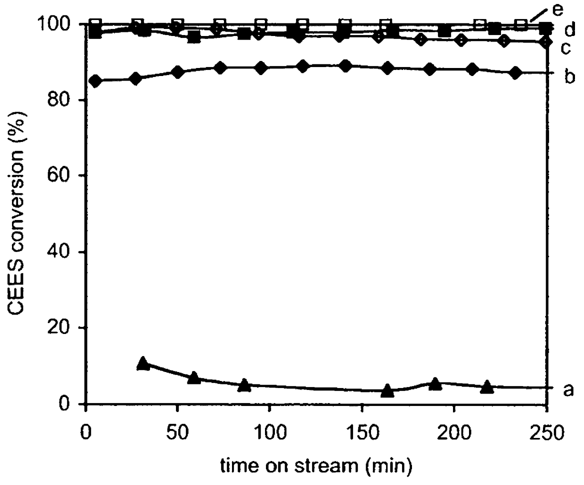
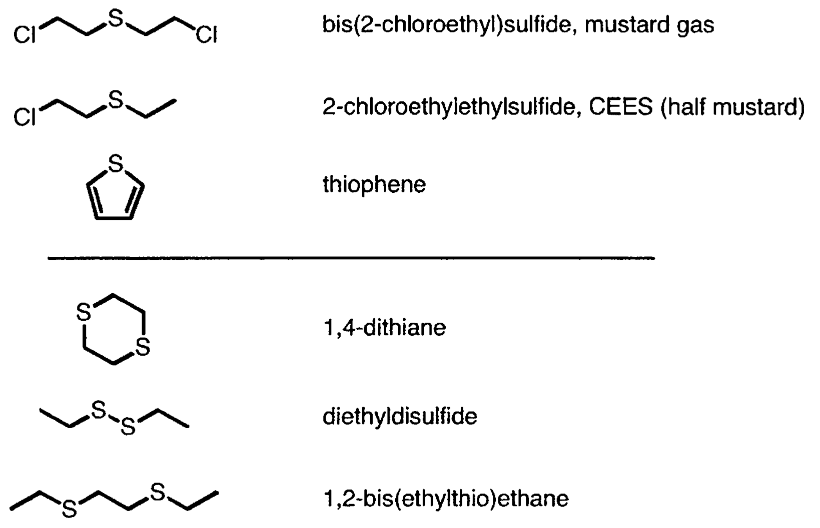


Figure 2. CEES conversions at 300 °C as a function of time for the same substrates shown in figure 1. In these experiments, the substrates were pre-sulfided in flowing H_2S prior to HDS.



Scheme 1. Top, mustard gas and simulants used for laboratory experiments. Bottom: selected products from HDS of CEES.

significant difference. MoS_2 has a well-known layered structure, and HDS activity is highest at the edges of the layers. Localization of Co at the edge sites is thought to increase catalytic activity [26]. Interestingly, elemental analysis of the substrates both after pre-sulfidation and after HDS still showed Mo:S molar ratios less than 2, indicating incomplete formation of MoS_2. It may be that Mo concentrations above 5% in the sample are required to produce discrete MoS_2 crystallites within the substrate that are observable by XRD. In these substrates therefore, it was not possible to determine the structural role played by Co. The activities of the substrates 5-Mo-30, 5-CoMo-30 and 2-CoMo-30 were essentially indistinguishable, and all showed conversions of at least 98%; one sample, 2-CoMo-30, showed 100% conversion at all times. The main products of CEES degradation (~75% of moles of total products) under these conditions were ethane, H_2S, and HCl; minor products (less than 10%) included ethanethiol, 1,2-bis(ethylthio)ethane, 1,4-dithiane, ethene, chloroethane, and diethyldisulfide (scheme 1). No oxygen-containing products were observed.

Since all catalysts showed essentially indistinguishable activities at 300 °C, HDS was repeated at 250 and 200 °C (figures 3 and 4). For comparison, a commercial CoMo-doped Al_2O_3 HDS catalyst (9 wt% Mo) was tested, and samples of APMS with comparable Mo loadings (10 wt%, with and without Co) were also tested. At 250 °C, 2-Mo-30 shows a significant drop-off in activity, while 2-CoMo-30 was significantly more active. This confirms the ability of Co to enhance the HDS activity of Mo for this level of Mo doping. Repeating the experiments at 200 °C in order to separate out the activities of the remaining catalysts shows that catalysts containing Co were indeed more active than samples containing Mo only, confirming literature results. Interestingly, 10-CoMo-30 consistently showed the highest activity of all samples tested, including the commercial sample. At 250 °C, it showed 100% conversion at all times, and it showed an appreciably higher conversion at 200 °C than the commercial sample. This was likely due to the enhanced surface area of the APMS substrate as compared to Al_2O_3(1050 m^2/g versus 210 m^2/g), which in turn led to a greater amount of catalyst per gram of substrate.

In conclusion, we have shown that APMS is an effective substrate for HDS of CEES and that pre-sulfidation is important in producing an effective catalyst. Pre-sulfida tion also introduce changes in the product distribution resulting from HDS of CEES. We have also confirmed that trace amounts of Co enhance the catalytic activity of Mo-doped APMS. Finally, APMS doped with Mo and Co shows a significantly higher activity than a

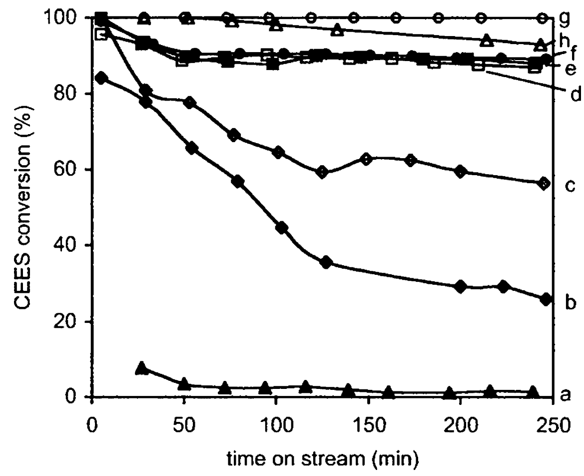


Figure 3. CEES conversions at 250 °C as a function of time. Samples were pre-sulfided prior to HDS. (a) Undoped APMS-30, closed triangles; (b) 2-Mo-30, closed diamonds; (c) 2-CoMo-30, open diamonds; (d) 5-Mo-30, closed squares; (e) 5-CoMo-30, open square; (f) 10-Mo-30, closed circles; (g) 10-CoMo-30, open circles; (h) commercial catalyst, $CoMo/Al_2O_3$, open triangles.

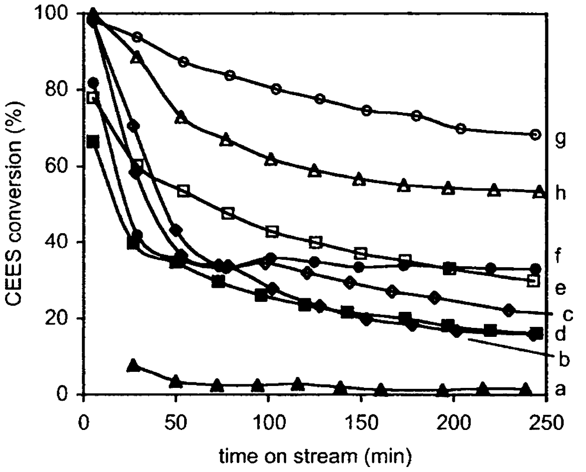


Figure 4 CEES conversions at 200 °C as a function of time for the same substrates shown in figure 3. Samples were pre-sulfided prior to HDS.

comparable commercial catalyst using Al_2O_3 as the substrate. Studies currently underway include an investigation of the effect of introducing Al into the APMS substrate on the HDS product distribution.

Acknowledgment

This work was supported by the Army Research Office under grant number DAAD19-03-1-0093.

References

[1] N.B. Munro, S.S. Talmage, G.D. Griffin, L.C. Waters, A.P. Watson, J.F. King and V. Hauschild, Res. Rev. 107 (1999) 933.
[2] L. Ember, Chem. Eng. News 68 (1990) 9.
[3] Y.-C. Yang, J.A. Baker and J.R. Ward, Chem. Rev. 92 (1992) 1729.
[4] Y.-C. Yang, Acc. Chem. Res. 32 (1999) 109.
[5] L. Ember, Chem. Eng. News 77(10) (1999) 10.
[6] G.W. Wagner, L.R. Procell, R.J. O'Connor, S. Munavalli, C.L. Carnes, P.N. Kapoor and K.J. Klabunde, J. Am. Chem. Soc. 123 (2001) 1636.
[7] G.W. Wagner, O.B. Koper, E. Lucas, S. Decker and K.J. Klabunde, J. Phys. Chem. B 104 (2000) 5118.
[8] J. Hirade and A. Ninomiya, J. Biochem. 37 (1950) 19.
[9] A.C. Sorensen, B.L. Fuller, A.G. Eklund and C.C. Landry, Chem. Mater. 16 (2004) 2157.
[10] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.
[11] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[12] K.W. Gallis, J.T. Araujo, K.J. Duff, J.G. Moore and C.C. Landry, Adv. Mater. 11 (1999) 1452.
[13] K.W. Gallis, A.G. Eklund, S.T. Jull, J.T. Araujo, J.G. Moore and C.C. Landry, Stud. Surf. Sci. Catal. 129 (2000) 747.
[14] K.W. Gallis and C.C. Landry, U.S. Patent 6,334,988 (2002)..
[15] K.W. Gallis and C.C. Landry, Adv. Mater 13 (2001) 23.
[16] D.K. Rohrbaugh, Y. Yang and R.J. Ward, J. Chromatogr. 417 (1988) 165.
[17] D. Panayotov and J.T. Yates Jr., J. Phys. Chem. B 107 (2003) 10560.
[18] B.W.L. Jang and J.J. Spivey, Catal. Today 55 (2000) 3.
[19] C. Topsøe, Catal. Rev.-Sci. Eng. 26 (1984) 395.
[20] E. Furminsky and C.H. Amberg, Can. J. Chem. 53 (1975) 2542.
[21] S. Fuentes, G. Diaz, F. Pedraza, H. Rojas and N. Rosas, J. Catal. 113 (1988) 535.
[22] C. Song and K.M. Reddy, Appl. Catal. A 176 (1999) 1.
[23] Mustard gas has a melting point of 13 °C and a boiling point of 218 °C. CEES has a boiling point of 156 °C (melting point unavailable)..
[24] J. Laine, Acta Cient. Venezolana 33 (1982) 121.
[25] W.P. Boone and J.G. Ekerdt, J. Catal. 193 (2000) 96.
[26] R. Prins, V.H.J. DeBeer and G.A. Somorjai, Catal. Rev.-Sci. Eng. 31 (1989) 1.
[27] J.R. Günter, O. Marks, T.I. Korányi and Z. Paál, Appl. Catal. 39 (1988) 285.
[28] Y. Morimura, S. Nakata, T. Takatsuka and M. Nakamura, Sekiyu Gakkaishi 38 (1995) 192.
[29] T.I. Korányi, V. Rozanov, R. Kremó and Z. Paál, J. Mol. Catal. 63 (1990) 31.