Surface Areas of the MoS_2-Based Catalysts

The surface areas of the catalysts were measured on a Gemini 2360 instrument using the BET multipoint method with nitrogen as the adsorbate. For the undoped MoS_2 catalyst, 10 data points were taken in the relative pressure range of $p/p_o = 0.05$ to $p/p_o = 0.30$ (see Figure 78), where p_o = saturated vapor pressure of N_2. For the rest of the samples, typically seven data points were obtained from $p/p_o = 0.05$ to $p/p_o = 0.30$ (e.g. see Figures 79 and 80). The plots show $z/[(1-z)V]$ *vs* z, where $z = p/p_o$, which are based on the BET equation of $p/[(p_o-p)V] = 1/V_mC + [(C-1)/(V_mC)]/(p/p_o)$, where V is the volume of gas adsorbed, V_m is the monolayer capacity, and C is the BET constant [90]. Multiplying V_m by the cross-sectional area of the N_2 molecule yields the specific surface area of the solid.

The surface areas of the undoped MoS_2 catalyst, the 20 wt% $CsOOCH/MoS_2$ catalyst prepared in air but before testing, and the Cs-doped catalyst after long-term testing were determined. These surface areas are compared with previously prepared and characterized catalysts in Table 14. The surface area of the undoped MoS_2 catalyst was found to be 60 m^2/g. This is comparable to the previously reported [11] surface area of a different preparation of the undoped MoS_2 catalyst of 63 m^2/g, which was obtained by heating MoS_3 in flowing N_2 to 500°C for 1 hr, using a heating rate of 10°C/min.

TABLE 14. Comparison of surface areas of the undoped MoS_2, untested 20 wt% $CsOOCH/MoS_2$, and tested 20 wt% $CsOOCH/MoS_2$ catalysts.

Catalyst	Surface Areas of Current Catalysts	Surface Areas of Earlier Catalysts [11]
MoS_2	60	63
Untested Cs/MoS_2	14	13
Tested Cs/MoS_2	6	--

FIGURE 78. BET Plot
For Undoped MoS_2

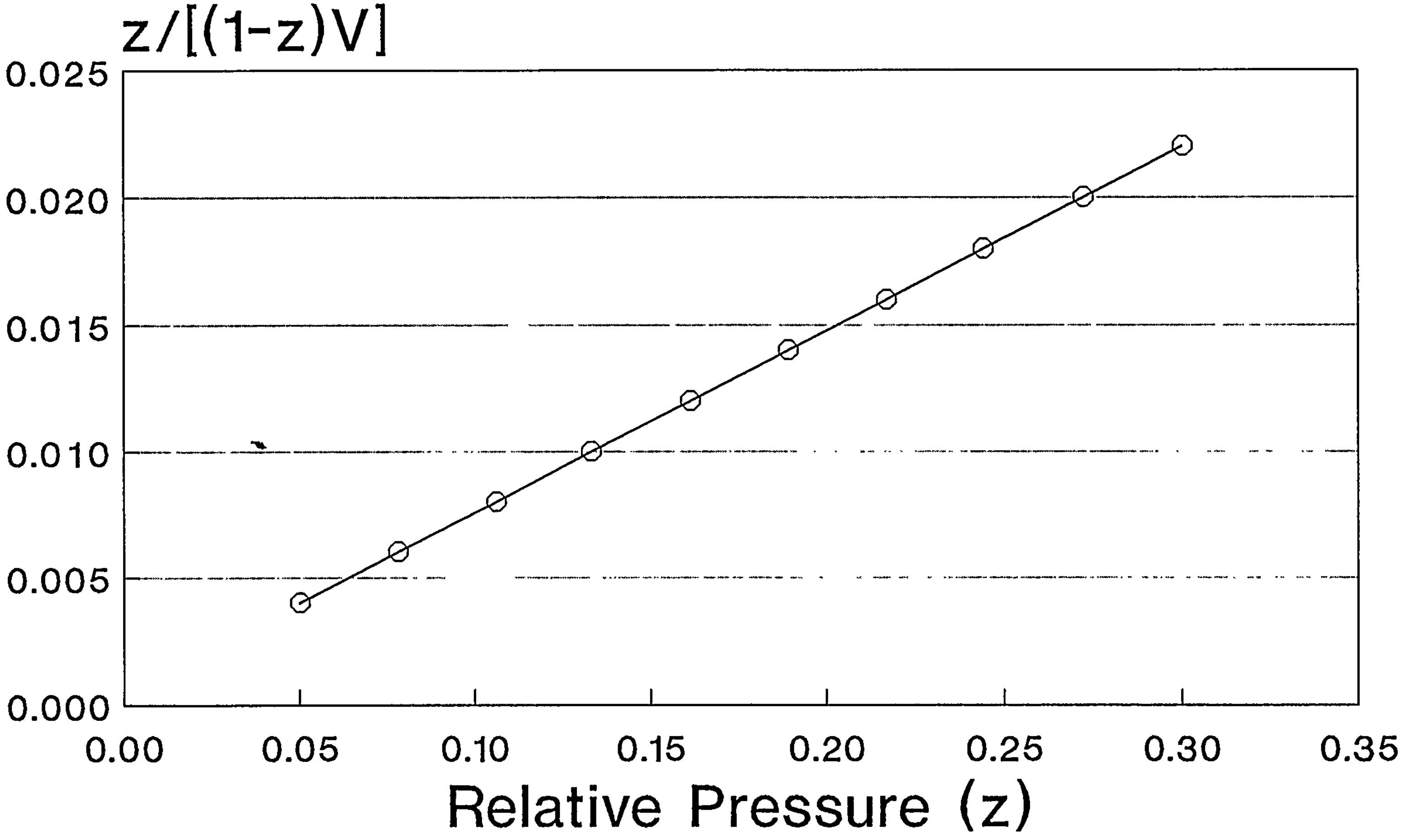


FIGURE 79. BET Plot For Untested 20wt% Cs/MoS_2

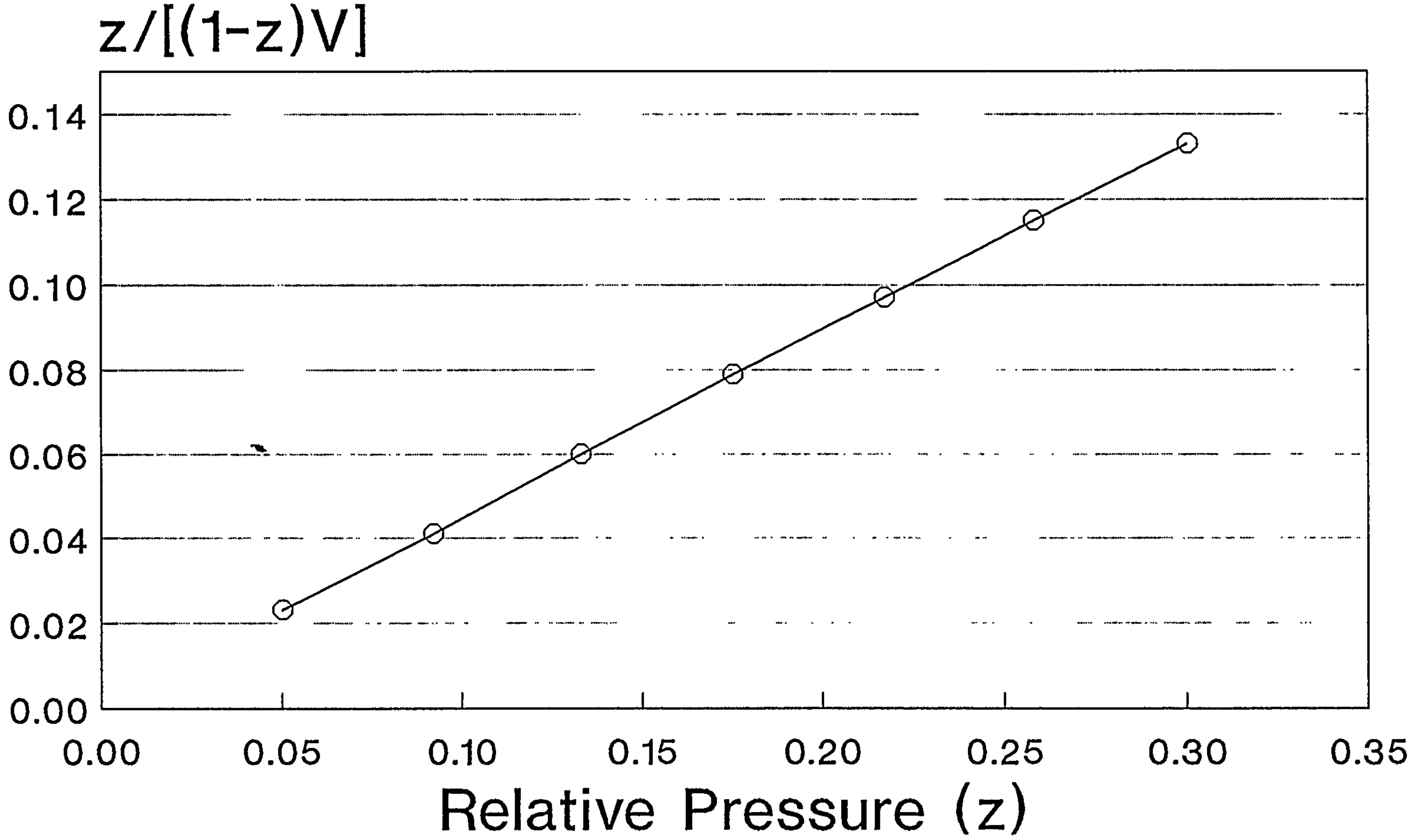
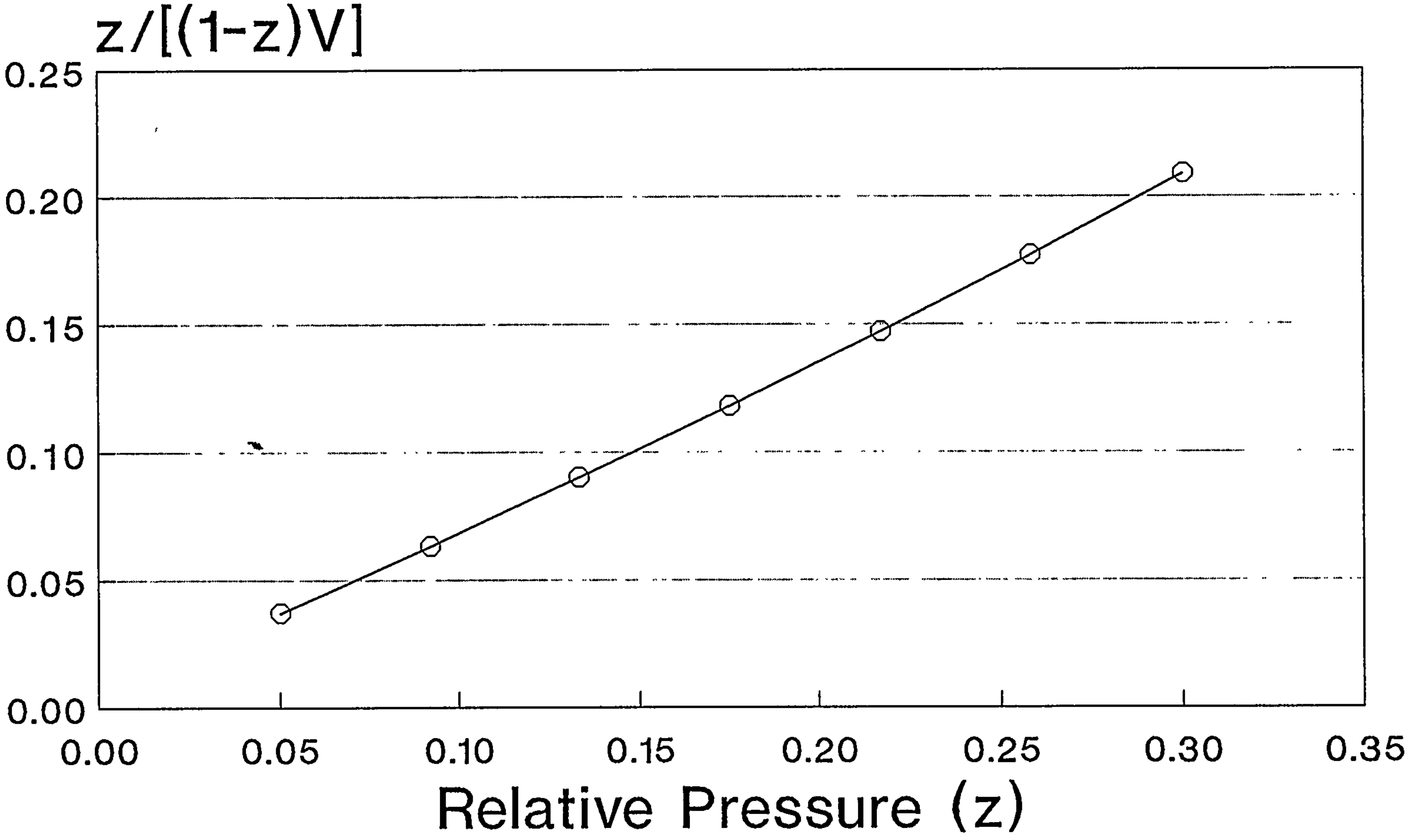


FIGURE 80. BET Plot for Tested 20 wt% Cs/MoS_2



The surface area of the 20 wt% CsOOCH/MoS_2 before catalytic testing, but after drying to 300°C, was found to be 14 m^2/g. This is also consistent with 13 m^2/g reported previously [11]. The surface area of the Cs-doped catalyst after testing decreased to 6 m^2/g. This decrease in surface area occurred over 551 hr of high temperature and high pressure conditions. Although a slight decrease in surface area to ≈11 m^2/g during catalyst testing was previously reported [65], the loss of surface area for the present catalyst was quite significant. One possible reason for this loss of surface area is that the cesium formate could have agglomerated on the surface during testing. This agglomeration, in turn, could have blocked the pores of the catalyst, thus giving a lower surface area. This agglomeration may have been more pronounced in this catalyst, because a different doping method was used. Previously, the doping was carried out in vacuum [11]. For the current catalyst, doping was done at atmospheric pressure in air. This latter procedure might not allow the cesium to disperse into the pores. In this case of lower dispersion, under reaction conditions the cesium component could have more easily agglomerated.

Higher Surface Area Catalysts. Two higher surface area catalysts were produced, one with a surface area of 96 m^2/g and another with 91 m^2/g. The synthesized MoS_3 used to produce these catalysts was the same as for the previous catalyst. For the 96 m^2/g MoS_2, approximately 2 g of MoS_3 was added with Pyrex beads to a quartz tube. The sample was flushed with nitrogen and then heated under nitrogen up to 210°C. This temperature was held for 10 min, and then the sample was heated up to 450°C at a rate of 13°C/min. This temperature was maintained for 1.5 hr. The sample was allowed to cool to room temperature under nitrogen, and then the sample was transferred from the quartz tube in air.

To obtain the MoS_2 with a surface area of 91 m^2/g, approximately 2 g of MoS_3 was added with Pyrex beads to the quartz decomposition tube. Under nitrogen flow, the sample was heated to 250°C and held there for 15 min. The sample was then heated at a rate of 15°C/min up to 460°C, and this temperature was maintained for 2 hr. The sample was allowed to cool to room temperature under nitrogen. The sample was transferred from the quartz tube to a sample vial in air.

The surface areas of these two samples were determined as described previously. The BET plots obtained with these samples are shown in Figures 81 and 82, and a linear relationship was again observed.

FIGURE 81. BET Plot for For 96 m^2/g MoS_2

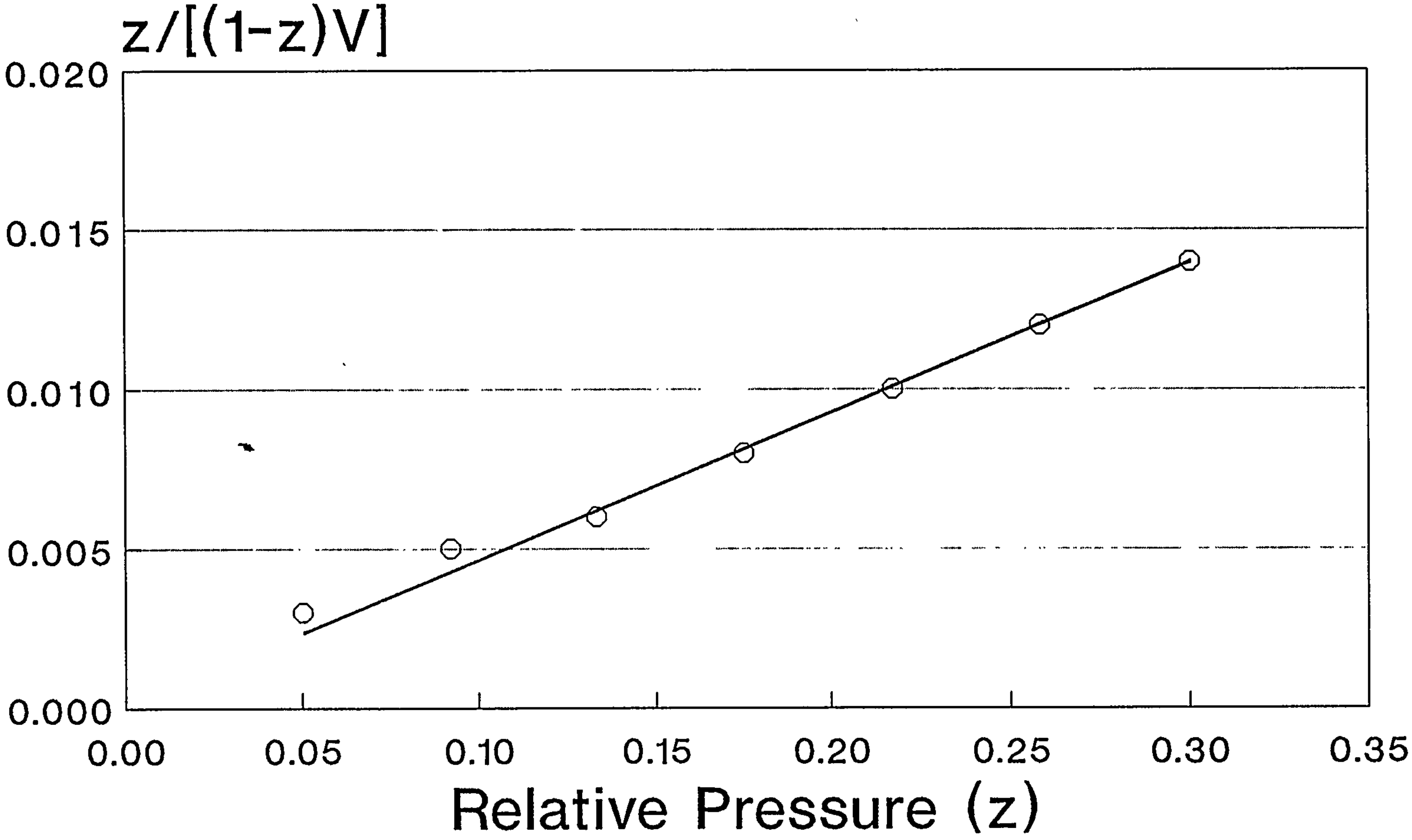
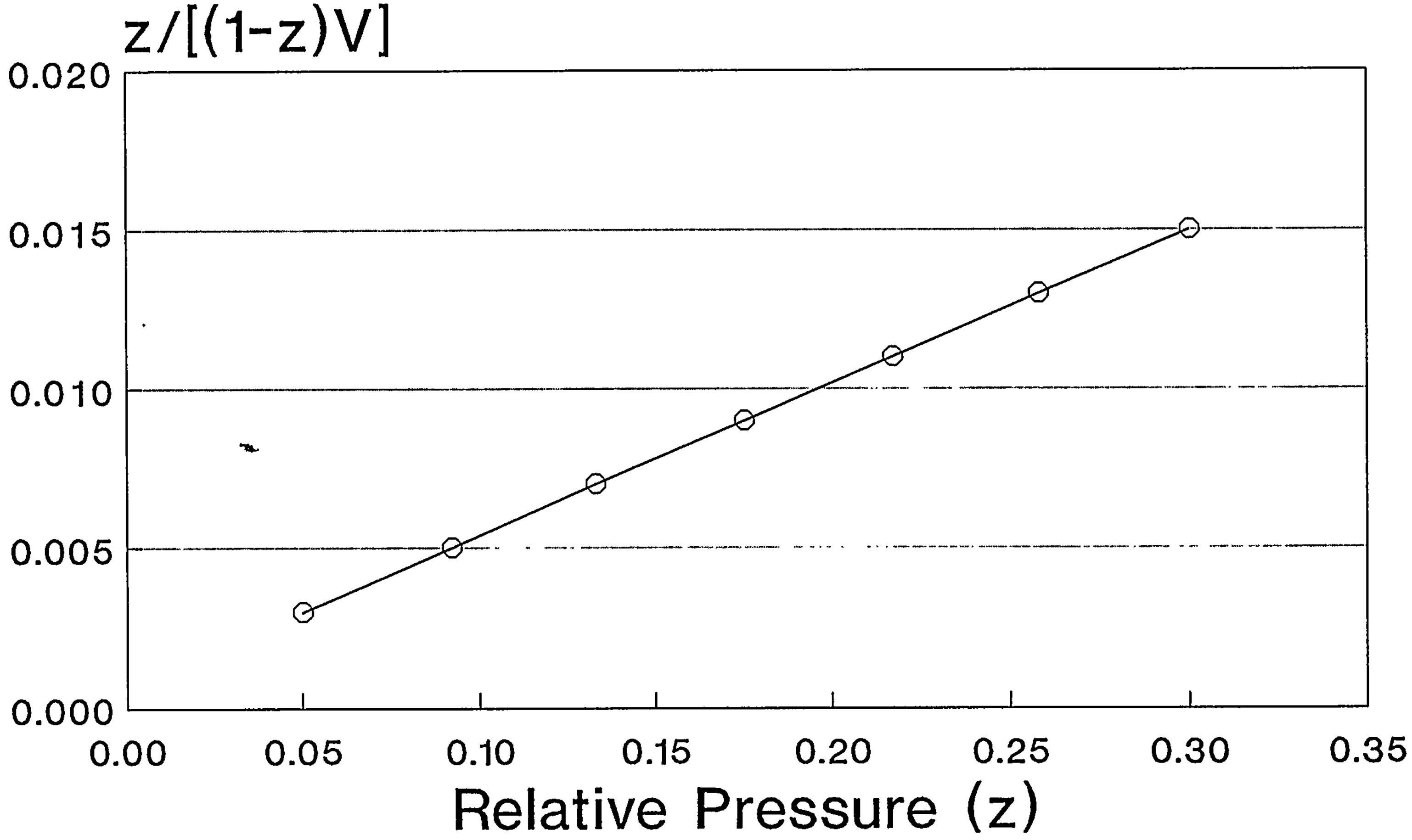


FIGURE 82. BET Plot For 91 m^2/g MoS_2



CONCLUSIONS

Computational studies were carried out in terms of the thermodynamic stability, the electronic structure, and redox properties of the sulfides of the transition metals in the early part of the periodic table. These analyses indicated that WS_2, ReS_2, and RuS_2, as well as MoS_2, should be stable catalysts under higher alcohol synthesis conditions. Thus, additional investigations should be carried out with these transition metal sulfides after surface doping with alkali metal cations, such as potassium and cesium.

It was shown that CsOOCH-doped MoS_2 catalysts can be reproducibly prepared and that reproducible catalytic behavior is observed with these materials. However, it was also shown that prolonged air exposure of the synthesized catalysts causes agglomeration of the CsOOCH dopant, leading to lower catalytic activity for the catalysts. Therefore, it is necessary to utilize freshly prepared catalysts protected from exposure to ambient air to obtain high alcohol synthesis activity Cs/MoS_2 catalysts. For example, with a fresh 10 wt% $CsOOCH/MoS_2$ catalyst, 300 g of linear alcohols/kg catal/hr were obtained from $H_2/CO = 1$ synthesis gas at 295°C, 8.3 MPa, and with GHSV = 7760 ℓ/kg catal/hr. Under our reaction conditions, the presence of H_2S in the synthesis gas was not necessary to obtain stable activity, but the presence of 45.5 ppm of H_2S in the synthesis gas did tend to decrease the space time yield of methane, especially at the higher reaction temperatures.

The new preparation procedures explored for doping the MoS_2 catalysts did not result in improved catalysts, and the optimum alkali content of the catalysts is still very high, i.e. 10-20 wt% CsOOCH. New preparation techniques need to be developed to improve the alkali dispersion on the catalysts so that the number of active sites is increased while decreasing the content of promoter needed.

REFERENCES

1. Kulakowski, M., Preprints, Div. Pet. Chem., ACS, 1994, 39(4), 494.

2. Gray, C. F., "EPA's Final RFG Regulation and Renewable Oxygenate Proposal," World Conference on Refinery Processing and Reformulated Gasoline, March 1994.

3. "Critical Technologies: The Role of Chemistry and Chemical Engineering," National Research Council, National Academy Press, Washington D. C., 1992, 22.

4. Piel, W. J.; Karas, L. J.; Kesling Jr., H. S., Preprints, Div. Pet. Chem, ACS, 1994, 39(4), 520.

5. Herman, R. G.; Klier K.; Feeley, O. C.; Johansson, M. A., Preprints, Div. Fuel Chem., ACS, 1994, 39(2), 343.

6. Klier, K.; Herman, R. G.; Johansson, M. A.; Feeley, O.C., Preprints, Div. Fuel Chem., ACS, 1992, 37(1), 236.

7. Herman, R. G.; Klier, K.; Young, C.-W.; Nunan, J. G.; Feeley, O.C.; Johansson, M.A., Proc. 9th Intern. Pittsburgh Coal Conf., 1992, 409.

8. Nunan, J. G.; Klier, K.; Herman, R. G., J. Catal., 1993, 139, 406.

9. Herman, R. G.; Klier, K.; Feeley, O.C.; Johansson, M.A.; Sun, Q.; Lietti, L., Preprints, Div. Fuel Chem., ACS, 1994, 39(4), 1141.

10. Feeley, O.C.; Johansson, M.A.; Herman, R. G.; Klier, K., Preprints, Div. Fuel Chem., ACS, 1992, 37(4), 1817.

11. Santiesteban, J. G., Ph.D. Dissertation, Lehigh University, Bethlehem, PA, 1989.

12. Cochran, G. A.; Conway, M. M.; Murchison, C. B.; Pynnonen, B. W.; Quarderer, Q. H.; Stevens, R. R.; Stowe, R. A.; Weihl, E. D., Intern.. Chem. Congr. Pac. Basin Soc., Honolulu, HI, 1984.; Quarderer, Q. J.; Cochran, G. A. Eur. Pat. Appl. 8,410,932.5 (March 16, 1984); assigned to Dow Chemical Co.

13. Kinkade, N. E. Eur. Pat. Appl. 84116467.6 and 84116468.4 (Dec. 28, 1984); assigned to Union Carbide Corporation.

14. Stevens, R. R. Eur. Pat. Appl. 84116467.6 (Dec. 28, 1984); Conway, M. M.; Murchison, C. B.; Stevens, R. R. Eur. Pat. Appl. 85109215.5 (July 23, 1985); Quanderer, G. J.; Cochran, G. A.; Stevens, R. R.; Murchison, C. B. Eur. Pat. Appl. 85109213.0 (July 23, 1985); Conway, M. M.; Murchison, G. B.; Stevens, R. R. U. S. Patent 4,675,344 (June 23, 1987); assigned to Dow Chemical Co.

15. Newsome, D. S., Catal. Rev.-Sci. Eng., 1980, 21(2), 279.

16. Fierro, J. L. G.; Gonzalez Tejuca, L.; Lopez Agudo, A.; Weller, S. W., J. Catal. 1984, 89, 111.

17. Chianelli, R. R.; Ruppert, A. F.; Behal, S. K.; Kear, B. H.; Wold, A; Kershaw, R., J. Catal., 1985, 92, 56.

18. Wise, H., Polyhedron, 1986, 5, 145.

19. Chianelli, R. R.; Daage, M., "Structure-Activity and Selectivity Relationships in Heterogeneous Catalysis," Elsevier: Amsterdam, 1991, p. 137.

20. Mross, W. D., Catal. Rev.-Sci. Eng., 1983, 25, 591.

21. Lee, G. v. D.; Ponec, V., Catal. Rev.-Sci. Eng., 1987, 29, 183.

22. Lee, J. S.; Kim, S.; Lee, K. H.; Nam, I.-S.; Chung, J. S.; Kim, Y. G.; Woo, H. C., Appl. Catal. A., 1994, 110, 11.

23. Woo, H. C.; Nam, I.-S.; Lee, J. S.; Chung, J. S.; Lee K. H.; Kim, Y. G., J. Catal., 1992, 138, 525.

24. Woo, H. C.; Kim, Y. G.; Moon, s. H.; Nam, I.-S.; Lee, J. S.; Chung, J. S., Huahak Konghak (J. Korean Inst. Chem. Eng.), 1990, 28, 552.

25. Woo, H. C.; Nam, I.-S.; Lee, J. S.; Chung, K. H.; Kim, Y. G., J. Catal., 1993, 142, 672.

26. Rosynek, M. P., J. Phys. Chem., 1975, 79, 1280.

27. Santiesteban, J. G.; Bogdan, C. E.; Herman, R. G.; Klier, K., in "Proc. 9th Intern. Congr. Catal.," Calgary (eds. M. J. Phillips and M. Ternan), The Chemical Institute of Canada: Ontario, Vol. 2, 1988, p 561.

28. Kennou, S.; Ladas, S.; Papageorgopoulos, C., Surf. Sci., 1985, 152/153, 1213.

29. Deluzarche, A.; Hindermann, J. P.; Kiennemann, A.; Kieffer, R., J. Mol. Catal., 1985, 31, 225.

30. Saussey, J.; Lavalley, J. C.; Lamotte, J.; Rais, T., J. Chem. Soc., Chem. Commun., 1982, 278.

31. Lavalley, J. C.; Saussey, J.; Rais, T., J. Mol. Catal., 1982, 17, 289.

32. Vedage, G. A.; Herman, R. G.; Klier, K., J. Catal., 1985, 95, 423.

33. Takeuchi, A.; Katzer, J. R., J. Phys. Chem., **1981**, 85, 937.

34. Veno, A.; Onishi, T.; Tamaru, K., Trans. Faraday Soc., **1971**, 67, 3585.

35. Blyholder, G.; Wyatt, W. V., J. Phys. Chem., **1966**, 70, 1745.

36. Kagel, R. O.; Greenler, R. G., J. Chem. Phys., **1968**, 49, 1638.

37. Soma, Y.; Onishi, T.; Tamaru, K., Trans, Faraday Soc., **1969**, 65, 2215.

38. Amenomiya, U.; Tagawa, T., "Proc. 8th Intern. Congr. Catal.", Berlin, Vol. 2, 1984, p 557.

39. Edwards, J. F.; Scrader, G. L., J. Catal., **1985**, 94, 175.

40. Bogdan, C. E., Ph.D. Dissertation, Department of Chemistry, Lehigh University, 1989.

41. Vedage, G. A.; Pitchai, R.; Herman, R. G.; Klier, K., in "Proc. 8th Intern. Congr. Catal.", Berlin, Vol. 2, 1984, p 47.

42. Frolich, P. K.; Cryder, D. S., Ind. Eng. Chem., **1930**, 22, 1051.

43. Graves, G. D., Ind. Eng. Chem., **1931**, 23, 1381.

44. Storch, H. H.; Columbic, N.; Anderson, R. B., "The Fischer-Tropsch Synthesis", Wiley: New York, 1951.

45. Anderson, R. B., in "Catalysis," (ed. P. H. Emmett), Reinhold: New York, Vol. 4, 1956, p 1.

46. Kummer, J. T.; Podgurski, H. H.; Spencer, W. D.; Emmett, P. H., J. Am. Chem. Soc., **1951**, 73, 564.

47. Hall, W. K.; Kokes, R. J.; Emmett, P. H., J. Am. Chem. Soc., **1957**, 79, 2983; **1957**, 79, 2989.

48. Fischer, F.; Tropsch, H., Brennstoff-Chem., **1923**, 4, 276; **1924**, 5, 201; **1924**, 5, 217.

49. Natta, G.; Colombo, U.; Pasquon, I., in "Catalysis," (ed. P. H. Emmett), Reinhold: New York, Vol. 5, 1957, p 131.

50. Kiennemann, A.; Hindermann, J. P., in "Catalysis on the Energy Scene," (eds. S. Kaliaguine and A. Mahay), Elsevier: Amsterdam, 1988, p 181.

51. Wender, I.; Levine, R.; Orchin, M., J. Am. Chem. Soc., **1949**, 71, 4160.

52. Henrici-Olivé, G.; Olivé, S., Angew. Chem. Int. Ed. Engl., 1976, 15, 136.

53. Pichler, H.; Schulz, H., Chem. Ing. Tech., 1970, 18, 1162.

54. Koga, N.; Morakuma, K., in "Transition Metal Hydrides," (ed. A. Dedieu), VCH Publishers: New York, 1992, Chapter 6.

55. Koga, N; Morokuma, K., Chem. Rev., 1991, 91, 823.

56. Nakamura, S.; Dedieu, A., Chem. Phys. Lett., 1984, 111, 243; and Dedieu, A.; Nakamura, S., in "The Challenge of Transition Metals and Coordination Chemistry," (ed. A. Veillard), NATO Advanced Study Institute Series, Reidel: Dordrecht, Vol. 176, 1981, p 277.

57. Rappé, A. K., J. Am. Chem. Soc., 1987, 109, 5605.

58. Fachinetti, G.; Floriani, D.; Marchetti, F.; Merlino, S., J. Chem. Soc., Chem. Commun., 1976, 522; Calderazzo, F., Angew. Chem. Int. Ed. Engl., 1977, 16, 299.

59. Berke, H.; Hoffmann, R., J. Am. Chem. Soc., 1978, 100, 7224.

60. Ziegler, T.; Versluis, L.; Tschinke, V., J. Am. Chem. Soc., 1986, 108, 612.

61. Axe, F. U.; Marynick, D. S., J. Am. Chem. Soc., 1988, 110, 3728.

62. Blomberg, M. R. A.; Karlsson, C. A. M.; Siegbahn, P. E. M., J. Phys. Chem., 1993, 97, 9341.

63. Barnett, K. W.; Beach, D. L.; Gaydos, S. P.; Pollman, T. G., J. Organomet. Chem., 1974, 69, 121.

64. Cotton, J. D.; Crisp, G. T.; Latif, L., Inorg. Chim. Acta., 1981, 47, 171.

65. Klier, K.; Herman, R. G.; Simmons, G. W.; Lyman, C. E.; Santiesteban, J. G.; Najbar, M.; Bastian, R., "Direct Synthesis of Alcohol Fuels over Molybdenum-Based Catalysts", Final Technical Report DOE/PC/80014-F, 1988.

66. Tonner, S. P.; Trimm, D. L.; Wainwright, M. S., J. Mol. Catal., 1983, 18, 215.

67. Reenwood, N. N.; Earnshaw, A., "Chemistry of the Elements," Pergamon Press: New York, 1990, p 424.

68. Klier, K.; Herman, R. G.; Himelfarb, P. B.; Young, C.-W.; Hou, S.; Marcos, J. A., in "New Frontiers in Catalysis," ed. by L. Guczi, F. Solymosi, and P. Tétényi, Elsevier and Akadémiai Kiadó, Budapest, Hungary, 1442, 1992.

69. Sachtler, W. M. H.; Shriver, D. F.; Hollenberg, W. B.; Lang, A. F., J. Catal., 1985, 92, 429.

70. Butts, S. B.; Holt, E. M.; Strauss, S. H.; Alcock, N. W.; Stimson, R. E.; Shriver, D. F., J. Am. Chem. Soc., 1979, 101, 5864.

71. Richards-Babb, M., Ph.D. Dissertation, Department of Chemistry, Lehigh University, 1992.

72. Klier, K.; Herman, R. G.; Richards-Babb, M.; Bastian, R.; Kieke, M., "Alkali/TX_2 Catalysts for CO/H_2 Conversion to C_1-C_4 Alcohols," Final Technical Report DOE/PC/88933-F, 1993.

73. Anderson, A. B.; Al-Saigh, Z. Y.; Hall, W. K., J. Phys. Chem., 1988, 92, 803.

74. Badger, E. H. M.; Griffith, R. H.; Newling, W. B. S., Proc. Roy. Soc. London, 1949, A197, 184.

75. Moyes, R. B., in "Hydrogen Effects in Catalysis," (Eds. Z. Paal; P. G. Menan), Dekker: New York, 1988, p 583.

76. Dianis, W. P., Appl. Catal., 1987, 30, 99.

77. Wright, C. J.; Sampson, C.; Fraser, D.; Moyes, R. B.; Wells, P. B., J. Chem. Soc., Faraday Trans. 1, 1980, 76, 1585.

78. Sampson, C.; Thomas, J. M.; Vasudevan, S.; Wright, C. J., Bull. Soc. Chim. Belg., 1981, 90, 1215.

79. Vasudevan, S.; Thomas, J. M.; Wright, C. J.; Sampson, C., J. Chem. Soc., Chem. Commun., 1982, 419.

80. Blackburn, A.; Serman, P. A., J. Chem. Tech. Biotechnol., 1983, 33A, 120.

81. Jones, P. N.; Knazinger, E.; Langel, W.; Moyes, R. B.; Tomkinson, J., Surf. Sci., 1988, 207, 159.

82. Komatsu, T.; Hall, W. K., J. Phys. Chem., 1991, 95, 9966.

83. Whangbo, M.-H.; Evain, M.; Hughbanks, T.; Kertesz, M.; Wijeyesekera, S.; Wilker, C.; Zheng, C.; Hoffmann, R., "Extended Hückel Molecular, Crystal and Properties Package," QCPE 571.

84. Barin, I.; Knacke, O., "Thermochemical Properties of Inorganic Substances," Springer-Verlag, New York, 1973.

85. Barin, I.; Knacke, O.; Kubaschewski, O., "Thermochemical Properties of Inorganic Substances-Supplement," Springer-Verlag, New York, 1977.

86. Mills, K. C., "Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides," Butterworths & Co., London, 1974.

87. Herman, R. G., in "New Trends in CO Activation," (ed. L. Guczi), Elsevier: Amsterdam, 265, 1991.

88. Conway, M. M.; Murchison, G. B.; Stevens, R. R., U. S. Patent 4,675,344 (June 23, 1987); assigned to Dow Chemical Co.

89. Bogdan, C. E.; Nunan, J. G.; Santiesteban, J. G.; Herman, R. G.; Klier, K., in "Catalysis-1987," (ed. J. W. Ward), Elsevier: Amsterdam, 745, 1988.

90. Herman, R. G.; Pendleton, P.; Bulko, J. B., in "Advances in Materials Characterization," Mater. Sci. Res. Vol. 15 (eds. D. R. Rossington, R. L. Condrate, and R. L. Snyder), Plenum Press: NY, 109, 1983.