JOURNAL OF CATALYSIS 49, 376–378 (1977)

NOTES

Diluent Gas Effect in SO_2 Oxidation over a Platinum–Alumina Catalyst

In this note we report an observation of a diluent gas effect on the rate of SO_2 oxidation over a platinum–alumina catalyst. Thus far, all observations of this curious effect for heterogeneous catalytic systems (*1–5*) have been with a vanadia catalyst.

For this series of experiments, the apparatus employed was that previously used by Rungta *et al.* (*4*) in their study of SO_2 oxidation over a vanadia catalyst. The analysis technique was also identical, except for a slight modification to improve the efficiency of the condensers. Two condensers in series containing pure water were used at room temperature to collect, respectively, 85 and 14.5% of the product. This method had the additional advantage of permitting SO_2 to be purged from solution with nitrogen in substantially less time than was required by Rungta *et al.* using an isopropyl alcohol and water mixture. Details are given by Silva (*5*).

The catalyst was 0.1% platinum on γ-alumina (Girdler T-309) catalyst obtained from Chemetron Corporation, Louisville, Kentucky. For use in the differential reactor employed in the study, a few pellets were crushed and a 40/50 US mesh fraction of the particles was used for a catalyst sample (average diameter 0.36 mm).

Runs were carried out at flow rates similar to those used by Rungta *et al.* (*4*). An 18-h period was allowed before the reaction rate was determined for each of the points in the figures. Past work indicates this is ample time for transient effects to disappear (*4*).

Calculations performed on the rates of reaction indicated the rates were not controlled by heat or mass transfer effects either at the particle surface or within the particle (*6–9*). Specifically, a test for the presence of a concentration gradient within the particles using a suitable criterion (*6*) and assuming a first-order reaction in the limiting reactant (SO_2) gave a quotient some 600 times less than the critical value. A similar test for a temperature gradient across the boundary layer using the criterion of Mears (*7*) gave a quotient about 300 times less than the critical value. Intraparticle thermal gradients (*8*) and interphase concentration gradients (*9*) (normally those least likely to be important) were likewise negligible. In addition, no evidence was found to suggest the presence of multiple steady states in the range of variables examined. Thus, we are confident that the reported rates of reaction are not disguised by transport effects.

The results shown in Figs. 1 and 2 were obtained on the same catalyst sample (0.400 g) and with 60% diluent by volume in the reaction mixture.

A reactant mole ratio of SO_2 to O_2 of 0.44 was used to obtain the rates given in Fig. 1. A difference of about 20% in the rate of oxidation between the two diluents, He and Ar, can be seen. Over a V_2O_5 catalyst, Rungta *et al.* (*4*) using a SO_2/O_2 ratio of 0.60 showed a difference of about 60% between the two diluents. In both

Copyright © 1977 by Academic Press, Inc.
All rights of reproduction in any form reserved.

ISSN 0021-9517

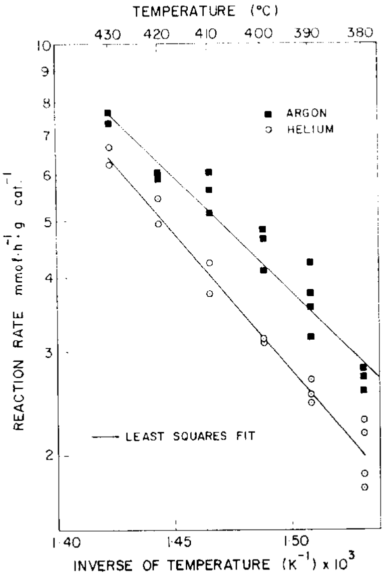

FIG. 1. Oxidation rate of SO_2 as a function of temperature at $p_{SO_2}/p_{O_2} = 0.44$. Total pressure = 120.0 kPa; diluent partial pressure = 72.2 kPa.

cases an Ar diluent provides the higher rate.

In Fig. 2, the SO_2/O_2 ratio has been increased to 1.76. At this ratio, there is no apparent difference between the rates of reaction with either diluent. Loss of the diluent effect at high SO_2/O_2 ratios was also observed for the V_2O_5 catalyst by both Rungta *et al.* (*4*) and Rhodey *et al.* (*2*).

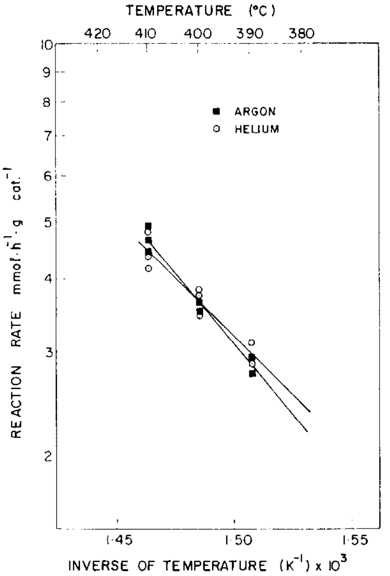

FIG. 2. Oxidation rate of SO_2 as a function of temperature at $p_{SO_2}/p_{O_2} = 1.76$. Other conditions as in Fig. 1.

TABLE 1

Apparent Activation Energies

Diluent gas	SO_2/O_2 mole ratio	Experimental value of E showing 95% confidence interval (kJ/mol)
He	0.44	73 ± 11
Ar	0.44	88 ± 9
He	1.76	76 ± 18
Ar	1.76	93 ± 18

Apparent activation energies for the runs in Figs. 1 and 2 are given in Table 1. There is a significant difference between the apparent activation energies at the SO_2/O_2 ratio of 0.44. At the higher SO_2/O_2 ratio, however, the difference is not significant. In addition, the activation energies are in approximately the same range as those obtained for He and Ar diluents by Rungta *et al.* (*4*).

Recent studies seem to agree that SO_2 oxidation over promoted V_2O_5 catalyst occurs by a redox mechanism (*10–13*). Controversy exists as to whether oxidation occurs by the same mechanism over Pt/Al_2O_3. It would seem unlikely, however, that the diluent gas effect is associated with just a redox mechanism. In a review paper, Hudgins and Silveston (*15*) argued that an adsorption interaction between the diluent and the solid phase is likely to be involved in an explanation of the diluent gas effect. Since adsorption is a fairly widespread phenomenon, we suggest, therefore, that the influence of diluent gases with catalytic reactions carried out previously over vanadia catalyst and now over Pt/Al_2O_3 is to be expected with other catalytic systems.

ACKNOWLEDGMENTS

The authors wish to acknowledge the financial support of the National Research Council of Canada in the form of research grants to R. R. Hudgins and P. L. Silveston and of the Petroleum Research Fund (5452-AC7) for partial support of this project. Catalyst was provided by Chemetron Corporation, Louisville, Kentucky.

REFERENCES

1. Baron, T., Manning, W. R., and Johnstone, H. F., *Chem. Eng. Prog.* **48**, 125 (1952).
2. Rhodey, W. G., Reilly, P. M., Silveston, P. L., and Hudgins, R. R., *J. Catal.* **42**, 312 (1976).
3. Yeramian, A. A., Silveston, P. L., and Hudgins, R. R., *Canad. J. Chem.* **48**, 1175 (1970).
4. Rungta, K. K., Hudgins, R. R., Silveston, P. L., *Canad. J. Chem.* **54**, 665 (1976).
5. Silva, A. E. M., Ph.D. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1976.
6. Hudgins, R. R., *Canad. J. Chem. Eng.* **50**, 527 (1972).
7. Mears, D. E., *J. Catal.* **20**, 127 (1971).
8. Anderson, J. B., *Chem. Eng. Sci.* **18**, 147 (1963).
9. Hudgins, R. R., *Chem. Eng. Sci.* **23**, 94 (1968).
10. Topsoe, F. A., and Nielsen, A., *Trans. Danish Acad. Technol. Sci.* **1**, 3 (1948).
11. Mars, P., and Maessen, J. E. H., *in* "Proceedings of the Third International Congress on Catalysis," Vol. 1, p. 266. North Holland, Amsterdam, 1965.
12. Holroyd, F. P. B., Ph.D. Thesis, Cambridge University, Cambridge, England, 1968.
13. Mezaki, R., and Kadlec, B., *J. Catal.* **25**, 454 (1972).
14. Dixon, J. K., and Longfield, J. E., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. 7, pp. 334–336. Reinhold, New York, 1960.
15. Hudgins, R. R., and Silveston, P. L., *Catal. Rev.-Sci. Eng.* **11**, 167 (1975).

ADOLFO EULOGIO MANUEL SILVA[1]
ROBERT ROSS HUDGINS
PETER LEWIS SILVESTON

Department of Chemical Engineering,
University of Waterloo,
Waterloo, Ontario,
Canada N2L 3G1

Received June 21, 1976; revised April 26, 1977

[1] Present address: Research Laboratories, Syncrude Canada, Edmonton, Alberta, Canada.