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Cubic Hypovanadate Perovskite as an Oxidation Catalyst

$SrVO_3$, a cubic perovskite binary oxide, has been investigated as a catalyst for the oxidation of methanol and of benzene. A comparison has been attempted between the catalytic activities and selectivities for the two reactions.

INTRODUCTION

Oxides with the perovskite structure have been used in the oxidation of CO to CO_2 (*1*), and in the oxidation–reduction reactions involved in the control of automotive exhaust emissions (*2–4*). Kinetic studies on oxidation of CO over perovskite titanates have also been carried out (*5*). Manganite perovskites have been found to have good activity for N_2O decomposition (*6*). However, systematic investigations on the catalytic behavior of vanadite and hypovanadate perovskites have not been reported except for a paper concerning the use of strontium hypovanadate ($SrVO_3$) as electrode material in anodic oxidation (*7*). $SrVO_3$ is a cubic perovskite with an expected susceptibility to oxidation at high temperatures. It can be easily reduced to $SrVO_{2.5}$ without any change in the perovskite structure (*8*). Mild oxidation of $SrVO_{2.5}$ to $SrVO_3$ or vigorous oxidation to *ortho-* or pyrovanadates of strontium may occur on exposure to a mixture of an organic compound, such as methanol or benzene, and air. If the former process occurs, $SrVO_3$ can be used as a redox catalyst. If the latter (vigorous oxidation) occurs, the perovskite cannot be used as catalyst. The present work aims at finding whether $SrVO_3$ is chemically stable under reaction conditions.

EXPERIMENTAL

$SrVO_3$ was prepared by heating a well-ground mixture of stoichiometric amounts of $SrCO_3$ and VO_2 in a vacuum furnace at 1000°C for 24 h with mixing at the end of every 6 h. This is a slight modification of the method adopted by Tofield (*9*) in that we have used VO_2 in place of V_2O_5 and hydrogen used by Tofield.

X-Ray powder diffraction patterns for the fresh and spent catalyst samples were obtained using a Dron-1 unit and CuK_α radiation with nickel filter. Estimation of V^{4+} in the sample was done by decomposing the sample with sulfuric acid and titrating the solution with 0.1 *N* potassium permanganate. Complete oxidation of the sample to $Sr_2V_2O_7$ supported by gravimetric studies established the composition as $SrVO_3$.

Catalytic activities for methanol and benzene oxidations were determined using a flow reactor at four temperatures—280, 320, 360, and 400°C; air was used in excess of what was required for complete oxidation (combustion). The feed rate of reactants and the flow rate of the gas stream over the catalyst were maintained at the same level for all the runs. Formaldehyde formed in the oxidation of methanol was estimated by iodimetry (*10*). Maleic anhydride produced in the oxidation of benzene was determined by titration against standard sodium hydroxide solution after boiling off CO_2 (*11*). CO_2 obtained in either oxidation was absorbed in a known excess of standard baryta solution and determined by residual method. Oxidative dehydrogenation of methanol over $SrVO_3$ in an argon atmosphere was also attempted with a view to ascertain whether $SrVO_3$ lends its lattice oxygen for oxidation in the absence of gas phase oxygen. Particle size and quantity of

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catalyst were small enough to prevent diffusional resistance in all the runs (*12*).

RESULTS

X-Ray diffraction pattern of the fresh catalyst showed lines which could be indexed to a cubic phase with a lattice constant of 3.84 Å. The diffractograms of the catalyst taken after use in the methanol oxidation at 320°C for 12 h did not show any lines other than those observed in the pattern for the fresh catalyst.

The results of the catalytic vapor phase oxidation of methanol are given in Tables 1 and 2. Oxidation of benzene vapor over this catalyst at 280, 320, 360, and 400°C yielded only CO_2 and very little maleic anhydride (Table 3). The spent catalyst is totally different from the fresh catalyst as regards benzene oxidation and $SrVO_3$ has been oxidized to $Sr_2V_2O_7$ after 12 h run. Results of methanol oxidation over $SrVO_3$ in argon atmosphere are given in Table 4.

Chemical analysis of the catalyst sample before use showed it to have 94% of the vanadium in the form of V^{4+}.

DISCUSSION

Though supported and unsupported vanadia are the catalysts of choice for the selective oxidation of aromatics (*13*), the reduction of the catalyst to an indefinite degree during use posed a problem in stabilizing the desired form of chemisorbed oxygen on the surface and hence in the improvement of selectivity. The fact that as many as seven oxide phases exist between V_2O_3 and V_2O_5 (*14*) deters all efforts at stabilizing the oxidation state of this element in a catalyst. Departures from stoichiometry which account for the coexistence of most of the above phases can be controlled only by incorporating the vanadium in an oxyanion. This has been realized in $SrVO_3$.

TABLE 1

Oxidation of Methanol over $SrVO_3$ at Different W/F Levels[a]

W/F[b]	Conversion (%)	Selectivity (%)
10.05	12.55	93.7
14.9	13.2	96.3
18	43.93	89.2

[a] Temperature: 320°C.

[b] $W/F = \dfrac{\text{weight of catalyst}}{\text{feed rate of methanol}}\ \text{g h mol}^{-1}$.

TABLE 2

Oxidation of Methanol over $SrVO_3$ at Different Temperatures[a]

Temperature (°C)	Conversion (%)	Selectivity (%)
280	18.58	94.9
320	43.93	89.2
360	27.14	95.98
400	15.47	93.7

[a] $W/F = \dfrac{\text{weight of catalyst}}{\text{feed rate of methanol}} = 18\ \text{g h mol}^{-1}$.

The results of the catalytic experiments on methanol oxidation show it to be a good catalyst. It brings about 44% conversion even at a moderate feed rate of methanol (Table 1). The high selectivity indicates that the unreduced catalyst has no bulk capacity

TABLE 3

Oxidation of Benzene over $SrVO_3$ at Different Temperatures[a]

Temperature (°C)	Conversion (%)	Selectivity[b] (%)
280	Nil	Nil
320	31.25	Nil
360	34.68	Nil
400	24.22	3

[a] $W/F = \dfrac{\text{weight of catalyst}}{\text{feed rate of methanol}} = 18\ \text{g h mol}^{-1}$.

[b] $$\begin{array}{l}\text{Selectivity (\%)}\\ \text{(to maleic}\\ \text{anhydride)}\end{array} = \frac{\begin{array}{c}\text{weight of benzene}\\ \text{converted into}\\ \text{maleic anhyd.}\end{array}}{\begin{array}{c}\text{weight of benzene}\\ \text{converted into}\\ \text{maleic anhydride}\\ \text{and } CO_2\end{array}} \times 100$$

TABLE 4

Oxidative Dehydrogenation of Methanol over $SrVO_3$ in an Argon Atmosphere at 320°C

Stage of the run	Conversion[a] (%)	Selectivity[b] (%)
During the first half-hour period	5	76
During the next half-hour period	1	Zero
After 1 h	Zero	Zero

[a] $$\text{Conversion (\%)} = \frac{\text{weight of methanol/benzene reacted}}{\text{weight of methanol/benzene fed}} \times 100$$

[b] $$\text{Selectivity (\%) (to HCHO)} = \frac{\text{weight of methanol converted into HCHO}}{\text{weight of methanol converted into HCHO and } CO_2} \times 100$$

to adsorb oxygen in the presence of methanol or formaldehyde. The difference in behavior of the catalyst in the two oxidations may possibly be due to the difference in the ease of oxidizability of the two substrate molecules (*15*). Further, deep oxidation being more exothermic than mild oxidation has caused the thermal decomposition of the catalyst during benzene oxidation.

The results of the catalytic experiments on methanol carried out in argon atmosphere as a substitute for the pulse technique are given in Table 4. If $SrVO_3$ spends its lattice oxygen for methanol oxidation, each gram of the catalyst should at the most oxidize about 0.17 g of methanol in the absence of oxygen. Our investigation pointed to a total conversion of only 0.06 g of methanol before the conversion level touched zero for want of oxygen. The difference is explained by the nonavailability of bulk O^{2-} ions and to the absence of anion mobility in this structure at 320°C. However, if lattice oxygen is not utilized, conversion should have been nil even from the beginning. Thus lattice oxygen participation is inferred which remains to be conclusively demonstrated in a pulse setup.

REFERENCES

1. Prakash, G., Ganguly, P., Rao, C. N. R., Rajoria, D. S., and Bhide, V. G., Mater. Res. Bull. **9,** 1173 (1974).
2. Libby, W. F., *Science* **171,** 499 (1971).
3. Voorhoeve, R. J. H., Remeika, J. P., Freeland, E., and Mathias, B. T., *Science* **177,** 383 (1972).
4. Voorhoeve, R. J. H., Remeika, J. P., and Johnson, D. W., Jr., *Science* **180,** 62 (1973).
5. Nagasubramanian, G., Viswanathan, B., and Sastri, M. V. C., *Indian J. Chem.* **16A,** 639–641 (1978).
6. Louis Raj, S., and Srinivasan, V., *J. Catal.* **65,** 121–126 (1980).
7. Matsumoto, Y., Yoneyama, H., and Tamura, H., *J. Electroanal. Chem.* **79,** 319–326 (1977).
8. Kestigian, M., Dickonson, J. G., and Ward, R. *J. Amer. Chem. Soc.* **79,** 5598 (1957).
9. Tofield, B. C., *Nature* (*London*) **272,** 713 (1978).
10. Frederic Walker, J., "Formaldehyde," p. 489, Reinhold, New York, 1964.
11. Antoni Inglot, *Bull. Acad. Pol. Sci.* **27,** 155 (1979).
12. Bond, G. C., "Heterogeneous Catalysis, Principles, and Applications," Oxford Univ. Press, 1974.
13. Vol'f'son, V. Ya, Zhigailo, Ya. V., Totskaya, E. F., and Raksha, V. V., *Kinet. Katal.* **6,** 138–142 (1965).
14. Kosuge, K., Toshio, T., and Kachi, S., *J. Phys. Soc. Japan* **18,** 318–319 (1963).
15. Vol'f'son, V. Ya., *Kinet. Catal.* **6,** 484 (1965).

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