

Behaviour of Oxide Catalysts During the Catalysed Reactions of Propan-2-ol

M. SUBRAHMANYAM & J. C. KURIACOSE

Department of Chemistry, Indian Institute of Technology, Madras 600036

Received 23 October 1976; accepted 2 February 1977

Oxidation catalysts used in the dehydrogenation of propan-2-ol are deactivated with use. A variety of single and binary oxides have been studied to determine the factors responsible for this deactivation. Some generalizations for screening oxidation catalysts for selectivity are indicated.

TRANSITION metal oxides, pure and mixed, are widely used in catalytic vapour phase oxidation^{1,2}. Since the early 1960's there has been much interest in the oxidative dehydrogenation and ammoxidation of mono-olefins to diolefins, aldehydes and nitriles³⁻⁵. The reaction mechanism of the oxidation of olefins such as propene and butene or of mixtures of propene and ammonia over catalysts such as bismuth molybdenum oxide combinations is considered to be reasonably well understood. However, a number of details in the mechanism remain uncertain. One of the important questions arising in the mechanistic studies of these reactions is the role of lattice oxygen in the oxidation, which in turn depends on the mobility of the oxide ions. The studies are difficult because of the many products involved in the reactions and the absence of information as to the adsorption equilibria of the various reactants and reaction products.

As a first step in a research meant to understand the factors controlling the activity, a number of oxides of different elements which have been used mostly for oxidation of olefins were tested for the decomposition of propan-2-ol in order to correlate the reaction of propan-2-ol to the selectivity of the catalyst for the oxidation of olefins. The reactions of propan-2-ol on these catalysts give rise to only a limited number of products unlike the oxidation of olefins.

Preparation of catalysts — All the chemicals were of BDH analar grade and used as received.

The following materials were used as starting materials: Nitrates were used for bismuth, cobalt and zirconium, chloride for antimony, ammonium metavanadate for vanadium and oxides for tungsten and molybdenum.

Antimony oxide was prepared by first converting antimony chloride to hydroxide by precipitation from an aqueous solution with ammonium hydroxide. The hydroxide was filtered, washed free of chloride with distilled water, dried at 130° and decomposed at 550° for 5 hr.

Vanadium pentoxide was prepared by three different methods: (a) Vanadyl oxalate was prepared from ammonium metavanadate and it was decomposed to oxide at 550°; (b) vanadic acid was precipi-

tated from ammonium metavanadate by nitric acid, dried and calcined at 550° for 5 hr; and (c) ammonium metavanadate was decomposed to vanadium pentoxide at 550° in a continuous stream of air.

Zirconium dioxide was prepared by precipitating the hydroxide from the nitrate with ammonium hydroxide and decomposing it at 550°.

For the preparation of binary oxides one of the oxides was suspended in boiling water and the other component in its hydroxide form added to the suspension. The total mass was stirred vigorously and was left on a water-bath for 1 hr after which it was filtered. The residue was dried overnight at 110° and calcined at 550° for 5 hr.

Reactions were carried out in a flow type reactor functioning at atmospheric pressure. The packing of the reactor and experimental procedure has been described in an earlier paper⁶. The catalyst was activated by heating it at 450° in a stream of dry air for 20 min. The liquid products were analysed by gas chromatography using a carbowax column at 75° and the gaseous products were analysed using an Orsat's apparatus⁶.

Results and Discussion

The results for the reaction of propan-2-ol on oxides of V, Mo, W, Co, Bi, Zr, Sb and Sn taken singly or in combination are presented in Tables 1 and 2. Most of these catalysts have attracted considerable attention in the past due to their effectiveness in the selective oxidation of hydrocarbons^{5,7,8}. Propan-2-ol undergoes both dehydrogenation and dehydration on these oxides.

The catalysts grouped in Table 1 undergo deactivation with reaction time until a low stable activity is reached. The percentage of acetone formed after the elapse of 5 min from the commencement of the reaction is given in Table 1. The catalysts grouped in Table 2 do not show a decrease in activity with time. In the case of Co/W mixtures, there was considerable carbon deposition even when oxygen was present in the feed. Antimony oxide and tin oxide were inactive.

The oxides in Table 1 serve as a source of oxygen as well as 'catalysts'. The catalytic activity declines with use due to oxygen depletion (reduction) in the oxide. Upon reoxidation of the aged catalyst

TABLE 1 — SALIENT FEATURES OF SOME OXIDATION CATALYSTS IN THE DECOMPOSITION OF PROPAN-2-OL

(Temp., 400°; contact time, 1 sec; wt of catalyst, 2 g)

| Catalyst* | | Acetone (%) per hr with duration (min) of run† | | |
|-------------------------------|-------|--|-------|-------|
| | | 5-10 | 25-30 | 40-45 |
| V ₂ O ₅ | (a) | 12 | 8 | — |
| | | 11 | 8 | — |
| | (b) | 25 | 15 | 5 |
| | | 25 | 14 | 5 |
| | (c) | 20 | 12 | 2 |
| | | 20 | 11 | 2 |
| Zr/Mo | (1:1) | 20 | 10 | 4 |
| | | 18 | 8 | 4 |
| | (7:3) | 18 | 10 | 2 |
| | | 17 | 11 | 3 |
| | (3:7) | 15 | 8 | 2 |
| | | 14 | 7 | — |
| Bi/W | (1:1) | 40 | 24 | 6 |
| | | 38 | 22 | 5 |
| Bi/V | (1:1) | 25 | 14 | 2 |
| | | 24 | 13 | 2 |
| V/Mo | (1:1) | 19 | 10 | 4 |
| | | 18 | 10 | 5 |

*Catalysts used show loss of activity with use. Both dehydrogenation and dehydration occurred on the catalysts.

†For each catalyst the second set of results is for the regenerated catalyst.

in air the initial activity is completely restored which can be seen from the duplicate values in Table 1. The loss of oxygen during reaction may be due to the relatively weak nature of the metal-oxygen bonds. In the mixed oxide systems in group A, mutual interaction between the oxides may be weakening the metal-oxygen bond. It has been shown that the energy of bonding of oxygen to a metallic oxide surface generally increases as oxygen is removed⁹ and correspondingly there is a decrease in dehydrogenation activity to a low value without the oxide being completely reduced.

Changes in the catalytic properties with composition in complex oxide systems are often associated with the formation of new compounds and solid solutions. For example, many authors¹⁰ who studied the activity of tin-antimony oxide catalysts for partial oxidation of olefins have shown that the active component in this system is a solid solution of antimony oxide in tin oxide while in the system Fe₂O₃-MoO₃ the active component has been shown to be normal iron molybdate¹¹. It was found that in the oxidative ammonolysis of propylene on bismuth-molybdenum catalysts, the most active composition corresponds to the compound Bi₂O₃·2MoO₃ (β-phase)¹².

The catalysts in Table 2, exhibiting a constant activity for dehydrogenation of propan-2-ol, can be considered to be true dehydrogenation catalysts since they aid in the removal of hydrogen without entering into a reaction with hydrogen. These oxides are not good catalysts for the partial oxidation of olefins¹³.

TABLE 2 — SALIENT FEATURES OF SOME OXIDATION CATALYSTS IN THE DECOMPOSITION OF PROPAN-2-OL

(Temp., 400°; contact time, 1 sec; wt of catalyst, 2 g)

| Catalyst* | Acetone (%) per hr with duration (min) of run | | | Type of reaction | |
|------------------|---|-------|-------|--|--|
| | 5-10 | 25-30 | 40-45 | | |
| ZrO ₂ | 4 | 3 | 3 | Mostly dehydration do Both dehydrogena- tion and dehydra- tion | |
| WO ₃ | 10 | 8 | 8 | | |
| ThO ₂ | 19 | 17 | 16 | | |
| Co/Mo | (1:1) | 40 | 38 | 36 | do |
| | (9:1) | 50 | 49 | 47 | do |
| | (7:3) | 43 | 42 | 40 | do |
| | (3:7) | 38 | 37 | 36 | do |
| | (1:9) | 30 | 29 | 28 | do |
| Zr/Mo | (9:1) | 10 | 10 | 9 | do |
| | (1:9) | 15 | 14 | 12 | do |
| Bi/W | (1:9) | 5 | 4 | 4 | do† |
| | (9:1) | 20 | 18 | 18 | do† |
| Co/W | (9:1) | 35 | 34 | 34 | do† |
| | (1:9) | 15 | 14 | 13 | do† |
| | (1:1) | 45 | 44 | 42 | do† |
| V/Mo | (9:1) | 6 | 5 | 5 | Mostly dehydration do |
| | (1:9) | 10 | 9 | 9 | |
| V/W | (1:1) | 15 | 14 | 14 | Both dehydrogena- tion and dehydra- tion |
| | | | | | |
| Sb/W | (1:1) | 10 | 9 | 8 | do |

*The catalysts employed do not show decrease in dehydrogenation activity with use.

†Visual inspection of aged catalyst showed that free bismuth oxide had got reduced to bismuth metal.

‡Lots of carbon deposit was observed even in the presence of oxygen in the feed.

 TABLE 3 — HEATS OF FORMATION OF OXIDES¹⁴

| Catalyst | $-\Delta H_{298} 10^{-6}$ J kg mole ⁻¹ | Catalyst | $-\Delta H_{298} 10^{-6}$ J kg mole ⁻¹ |
|--------------------------------|--|-------------------------------|--|
| Bi ₂ O ₃ | 577.778 | ThO ₂ | 1227.570 |
| SnO ₂ | 581.128 | ZrO ₂ | 1086.246 |
| Sb ₂ O ₃ | 699.614 | V ₂ O ₅ | 1559.583 |
| WO ₃ | 840.877 | | |

One may consider that for selective oxidation the energy of bonding of oxygen to the catalyst should not be too low since then the target products will be further oxidized rapidly. For example, Bi₂O₃ is reduced to metal by propan-2-ol at 400° giving rise to CO₂ and H₂O (ref. 13). On the other hand, if the bonding is too strong, the oxygen will not be available for reaction at all. The heats of formation of the relevant oxides are given in Table 3.

TABLE 4 — CORRELATION BETWEEN OXYGEN MOBILITY AND SELECTIVITY¹⁶

| Catalyst | Mobility | Selectivity to acrolein |
|-----------------------------|----------|-------------------------|
| Fe-Mo (industrial catalyst) | High | Low |
| Bi-Mo | Low | High |
| Bi-Mo=1 (Erman phase) | High | Low |
| Mn-Mo | Low | High |
| MoO ₃ | High | Low |
| Co-Mo | High | Low |

The heat of formation of ThO₂ and ZrO₂ are nearly equal and they do not undergo reduction while promoting the dehydrogenation of propan-2-ol, whereas V₂O₅ in spite of its higher heat of formation undergoes reduction while dehydrogenating propan-2-ol. Further, the heats of formation of SnO₂ and Sb₂O₃ are nearly equal and they are found to be inactive for dehydrogenation of propan-2-ol, whereas Bi₂O₃ which has a heat of formation almost equal to that of the above two oxides undergoes complete reduction to metal and oxidizes propan-2-ol to carbon dioxide and water.

If the heats of formation of oxides can be taken as a measure of the strength of the metal-oxygen bond, the above observation leads to the conclusion that the strength of the metal-oxygen bond cannot be the only factor responsible for the selectivity of the catalyst. However, Trifiro *et al.*¹⁵ have shown a relationship between selectivity of an oxide for the oxidation of propylene and mobility of lattice oxygen. The lattice oxygen mobility was determined by isotope exchange studies.

Molybdates with very mobile lattice oxygen are not selective in the oxidation of propylene, in contrast to those with moderately mobile lattice oxygen (Table 4). According to Trifiro *et al.* for selective oxidation the oxygen mobility must have an optimum value.

The dehydrogenation catalysts listed in part A function through a redox mechanism of the oxy-reductive type¹⁷. The oxygen reacts with hydrogen during the dehydrogenation. As to the mechanism of the reaction on the purely dehydrogenating catalysts, the first stage here too must be an interaction of the molecule to be reduced with the oxygen of the catalysts, but the oxygen is not consumed. This behaviour of the second group corresponds to a simple dehydrogenation mechanism.

Oxides which dehydrogenate propan-2-ol through an oxyreductive mechanism without getting reduced to the metallic state are also effective catalysts for the selective oxidation of olefins while those that are purely dehydrogenating do not function as oxidation catalysts.

References

1. BORESKOV, G. K., *Adv. Catalysis*, **15** (1964), 285.
2. TRIFIRO, F. & PASQUON, I., *J. Catalysis*, **12** (1968), 412.
3. SAMPSON, R. J. & SHOOTER, D., *Oxidation combustion review*, **1** (1965), 223.
4. VOGEL, H. H. & ADAMS, C. R., *Adv. Catalysis, related subjects*, **17** (1967), 151.
5. SKARCHENKO, V. K., *Russian chem. Rev.*, **37** (1968), 1.
6. KURIACOSE, J. C., DANIEL, C. & SWAMINATHAN, R., *Indian J. Chem.*, **7** (1969), 367.
7. HABER, J., *Intern. chem. Engng*, **15** (1975), 21.
8. GERMAIN, J. E., *Intra-Science Chem. Rept*, Vol. 6, 1972, 3.
9. BORESKOV, G. H., *Kinetika Kataliz*, **8** (1967), 1020.
10. GODIN, G., MAK-KEIN, K. K. & PORTER, E. A., *Proceedings of the Fourth International Congress on Catalysis*, Preprint of report No. 20, Moscow, 1968.
11. BORESKOV, G. K., KOLOVERTNOV, L. M., KEFELI, L. M. & PLYASOVA, L. M., *Kinetika Kataliz*, **7** (1966), 144.
12. KOLCHIN, I. K., MARGOLIS, L. YA. & BOBKOV, S. S., *Neftekhimiya*, **4** (1964), 301.
13. DANIEL, C., SUBRAHMANYAM, M. & KURIACOSE, J. C., *Indian J. Chem.*, **13** (1975), 419.
14. SAMSONOV, G. V., *The oxide hand book* (IFI/Plenum).
15. TRIFIRO, F., CENTOLA, P., PASQUON, I. & JIRU, P., *Proceedings of the Fourth International Congress on Catalysis*, Paper 18, Moscow, 1968.
16. TRIFORO, F. & PASQUON, I., *La Chimica L'Industria*, **53**, N. 6, Giugno, 1971.
17. KEULKS, G. W., *J. Catalysis*, **19** (1970), 232.