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The Effect of the Oxygen Content in a Series of Manganese Oxide Catalysts on Their Catalytic Activity and Selectivity in the Decomposition of Isopropyl Alcohol

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The catalytic decomposition of isopropyl alcohol vapor has been investigated from 35 to 280°C in a flow reactor on manganese oxides of compositions varying from MnO to Mn_2O_3. The catalytic reaction products have been identified and the catalyst selectivity in dehydrogenation and dehydration calculated from the values of the reaction rates. The apparent activation energy for dehydration between 156 and 280°C varies with the oxygen content in the catalyst series based on MnO, from 50 ± 2, stoichiometric MnO, to 56 ± 2 kcal mole^{-1}, $MnO_{1.3}$. Two distinct apparent activation energy regions occur for the dehydrogenation reaction. Between 150 and 200°C, the values lie from 5 to 8 kcal mole^{-1} while above 200°C these become 26 to 28 ± 1 kcal mole^{-1}. Stoichiometric Mn_2O_3 shows no dehydration activity and yields an apparent activation energy in dehydration of 15 ± 1 kcal mole^{-1} between 35 and 85°C.

In the discussion emphasis is placed on the role of the surface oxygen in the decomposition reactions and an interesting relationship established between the oxygen content of the catalyst and its activity in dehydrogenation.

INTRODUCTION

In a recent communication (*1*) the results of a study of catalytic activity and selectivity of manganese(II) oxide in the decomposition of isopropyl alcohol were reported. Both dehydration and dehydrogenation reactions were shown to occur simultaneously and although these reactions predominate, condensation occurs also to a detectable extent. This study has been extended to an examination of the higher oxides of manganese for which the literature data regarding their selectivity and activity in this and similar reactions are inconclusive (*2, 3*). For example, it has been reported (*2*) that the specific activities of MnO_2, Mn_2O_3 and MnO do not differ significantly in isopropyl alcohol decomposition while it has been concluded recently (*4*) that in a redox-type reaction, the decomposition of N_2O, the catalyst activity depends on the valence state of the metal cations. There are also indications that oxide-type catalysts may reach a stationary composition in the course of the reaction which can differ from the initial stoichiometry and which depends on the reaction temperature (*3, 5, 6*).

In an attempt to clarify these various findings, a detailed study of the catalytic properties of manganese(III) oxide and, more particularly, manganese(II) oxide has been carried out. Careful attention has been given to the influence of deviations from stoichiometry or the degree of reduction of the oxide on its activity and selectivity in the vapor-phase decomposition of isopropyl alcohol.

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EXPERIMENTAL METHODS

Apparatus and method. The flow system and general experimental procedures have been described (*1*). High-purity nitrogen was used as the carrier gas at atmospheric pressure.

The organic reaction products were analyzed at 80°C by a Beckman GC5 gas chromatograph with a hydrogen flame ionization detector using stainless-steel columns, 72 × 0.125 in. o.d., packed with "Carbowax 1540" on "Teflon 6," with nitrogen as the carrier gas. Carbon dioxide, water and hydrogen were analyzed by a thermal conductivity detector at 145°C using stainless-steel columns, 72 × 0.125 in. o.d., packed with "Porapak Q." The amplifier output on any given attenuation, from 1024×10^4 to 1, could be measured with a minimum accuracy of ±0.2% and the limit of detection for acetone and propylene was 0.005 and 0.002 ppm, respectively.

Surface areas were determined by low-temperature krypton adsorption (BET; $-196°\text{C}$; $\sigma = 21.5\ \text{Å}^2$).

Materials

a. Manganese(III) oxide. The method of preparation has been described (*1*). All other catalysts were prepared by reducing this material in 9.37 mm partial pressure isopropyl alcohol, at a flow rate of 300 ml min^{-1} (NTP), for 12 hr at the temperatures given in Table 1. For chemical analysis (*7*), the oxides were dissolved in 2 *M* nitric acid solutions containing 0.1% (w/v) ascorbic acid. Ten milliliters of 10% (v/v) triethanolamine solution were then added and the solutions buffered to pH 10. "Eriochrome black T" was used as the indicator in the subsequent titrations.

b. Reagents. Isopropyl alcohol was "Spectrosol" quality and its ultraviolet absorption characteristics, Unicam SP 800A, were the same as those given on its accompanying certificate. Nitrogen (Canadian Liquid Air Ltd.) was 99.99% pure.

RESULTS

The effect of temperature on the initial reaction products. One gram of manganese(III) oxide was raised to the reaction temperature in a 60 ml min^{-1} (NTP) stream of nitrogen before admission of isopropyl alcohol to the reactor. Experiments were then carried out with 9.37 mm partial pressure isopropyl alcohol at various fixed temperatures from 160 to 350°C at a total flow rate of 300 ml min^{-1} (NTP). The partial pressures of hydrogen, carbon dioxide and water vapor formed during the reaction were measured. Figure 1 shows the results at 350°C which typifies both the products and the reaction pattern obtained in these experiments. No attempt was made to measure quantitatively the amounts of acetone and propylene formed and no carbon monoxide was detected.

After each experiment the pyrophoric catalysts were cooled to room temperature in nitrogen at 60 ml min^{-1} (NTP) before removal from the catalyst reactor in order to prevent spontaneous oxidation.

Samples of the manganese oxide cata-

TABLE 1

PROPERTIES OF THE MANGANESE(III) OXIDE CATALYSTS AFTER REDUCTION AT DIFFERENT REACTION TEMPERATURES FOR 12 hr WITH ISOPROPYL ALCOHOL; PARTIAL PRESSURE ISOPROPYL ALCOHOL, 9.37 mm; FLOW RATE, 300 ml min^{-1} (NTP)

Sample no.	Temp of reaction (°C)	X-Ray diffraction analysis	Chemical analysis	Color	Surface area ($\text{m}^2\ \text{g}^{-1}$)	Time lapse to steady activity level (min)	Carbon dioxide in reduction products
1	350	MnO (only)	$MnO_{1.0}$	Black	14.0	60	Present
2	299	MnO (only)	$MnO_{1.0}$	Black	17.0	140	Present
3	253	MnO (+ trace Mn_2O_3)	$MnO_{1.2}$	Black	17.0	80	Present
4	207	Mn_3O_4 (only)	$MnO_{1.3}$	Brown	16.0	120	Absent
5	161	Mn_2O_3 (only)	$MnO_{1.5}$	Black	14.0	30	Absent

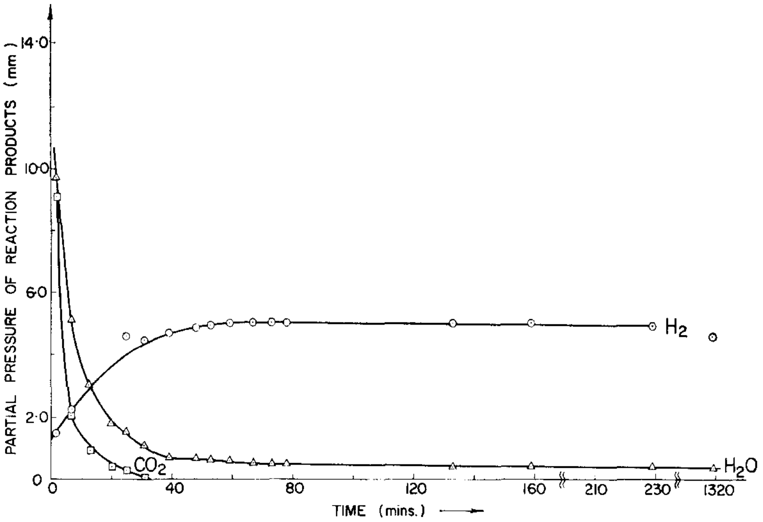

FIG. 1. Decomposition products of isopropyl alcohol (9.37 mm) on Mn_2O_3 at 350°C (excluding acetone and propylene).

lysts were examined by the X-ray powder diffraction technique. For samples used at 299 and 350°C the only X-ray pattern obtained was that of manganese(II) oxide, consistent with the results of chemical analysis. However, the sample still contained enough excess oxygen to retain the black color associated with manganese(III) oxide (*8*). After runs at 253°C the catalyst was composed principally of manganese(II) oxide but the two strongest X-ray diffraction lines for manganese(III) oxide were also present. These data were in accord with earlier results (*8*) while chemical analysis indicated $MnO_{1.2}$ as the composition of the oxide. Table 1 records the results of X-ray and chemical analysis, and surface area measurements made after 12-hr exposure of the various samples to isopropyl alcohol as well as the time taken to achieve the steady activity levels from first exposure. In runs at 161°C hydrogen could not be detected in the reaction products after an initial time lapse of 8 to 10 min.

The effect of oxygen content on activity. In these experiments a calculated amount of the oxide sample was introduced to the reactor to give 1 g of the final manganese oxide catalyst and a flame ionization detector was used to measure the rates of formation of acetone and propylene.

Preliminary runs confirmed (*1*) that external transport effects were not operative for flow rates between 200 and 500 ml min^{-1} (NTP) at temperatures from 30 to 280°C with an initial isopropyl alcohol partial pressure of 9.37 mm. All subsequent experiments were carried out with a flow rate of 300 ml min^{-1} (NTP). The grain size of the oxide catalysts was standardized at <0.1 mm since it was established that the reaction rates did not vary within the grain size range <0.05 to 0.15 mm. No evidence of particle aggregation was obtained under the conditions of the experiments.

A mass balance could be obtained for all catalytic runs at 220°C and above. For example with sample 1, Table 1, at 280°C and 9.37 mm isopropyl alcohol partial pressure, i.e., a feed rate of 282×10^{-8} mole sec^{-1} isopropyl alcohol, the effluent rates of acetone, propylene and unreacted isopropyl alcohol from the reactor were, respectively, 20.1, 4.1 and 258 mole $\text{sec}^{-1} \times 10^{-8}$. For all other runs the small amount of isopropyl alcohol reacted, $<0.5\%$, did not warrant the establishment of a mass balance. Reaction rates were calculated (*9*) from the amount of product detected, the flow rate (α 1/contact time) and the surface area of the sample, in the usual way. Although Table 1 shows that the

TABLE 2

REACTION RATES (mole m^{-2} sec^{-1} × 10^{11}) AND APPARENT ACTIVATION ENERGIES (kcal $mole^{-1}$) FOR DEHYDROGENATION (r_1) AND DEHYDRATION (r_2) OF ISOPROPYL ALCOHOL ON MANGANESE OXIDE CATALYSTS; PARTIAL PRESSURE ISOPROPYL ALCOHOL, 9.37 mm; FLOW RATE, 300 ml min^{-1} (NTP)

Sample no.	Temp of reduction	Rate (at 250°C) of: Dehydrogenation ($r_1 \times 10^{11}$)	Rate (at 250°C) of: Dehydration ($r_2 \times 10^{11}$)	Selectivity at 250°C $r_1/(r_1 + r_2)$	Activation energy for (kcal $mole^{-1}$): Dehydrogenation	Activation energy for (kcal $mole^{-1}$): Dehydration
1	350	339	51.3	0.87	28 ± 1 (280–200°C) 8 ± 1 (200–180°C)	50 ± 2 (280–180°C)
2	299	380	32.4	0.92	27 ± 1 (280–220°C) 5 ± 1 (190–160°C)	53 ± 2 (280–160°C)
3	253	447	32.4	0.93	26 ± 1 (250–210°C) —	55 ± 2 (250–200°C)
4	207	180 (200°C)	5.0 (200°C)	0.97 (200°C)	26 ± 1 (210–190°C) 8 ± 1 (180–150°C)	56 ± 2 (210–150°C)
Mn_2O_3	—	1.52 (50°C)	0.0 (50°C)	1.00 (50°C)	15 ± 1 (85–35°C)	No activity (85–35°C)

steady level of activity was reached in all cases within 3 hr, nevertheless, all samples were exposed to isopropyl alcohol vapor for 12 hr to establish the steady activity values used in the reaction rate calculations.

The precise effects of isopropyl alcohol and product concentrations on the reaction rates of both dehydrogenation and dehydration were examined as described previously (*1*) to confirm the general trends observed with respect to these components for the reaction at 323°C on "green" MnO. The dehydrogenation reaction showed no rate dependence on the concentration of any of the components and rate constants were calculated on the basis of an overall zero order reaction. The dehydration reaction showed a rate relationship $\alpha\ c_{H_2O}^{-0.5}$ and all other components had no influence. These rate constants were calculated by integration of the rate equation using an IBM 360/50 computer and the values obtained used in the Arrhenius plots to determine the apparent activation energies.

Both dehydration and dehydrogenation reactions occurred on all samples except Mn_2O_3 which showed dehydrogenation activity only. The results are summarized in Table 2 where the reaction rates for both dehydrogenation (r_1) and dehydration (r_2) are compared. The catalyst selectivities for dehydrogenation as well as the apparent activation energies for both reactions are also tabulated.

Figure 2 shows the Arrhenius plots used to calculate the apparent activation energies for oxide samples 1 and 2. The dehydrogenation plots have each two distinct regions with apparent activation energies of 27 ± 1 followed by 8 ± 1 kcal mole^{-1} (No. 1) and 28 ± 1 followed by 5 ± 1 kcal mole^{-1} (No. 2). The apparent activation energy for the dehydration reaction lies between 50 and 53 ± 2 kcal mole^{-1} over the entire temperature range for both samples. Similar Arrhenius plots were drawn for the reactions on all other samples.

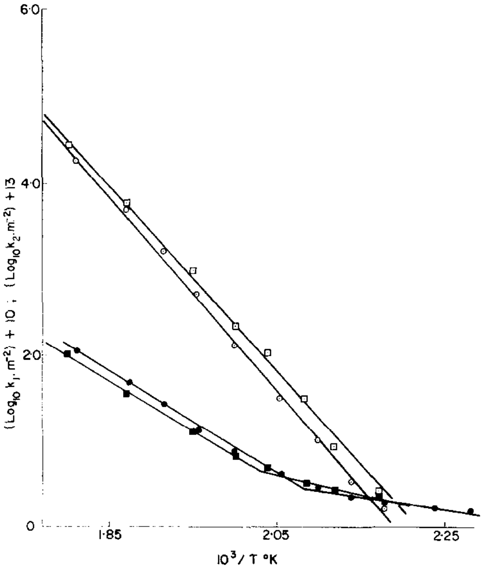

FIG. 2. Arrhenius plots for isopropyl alcohol decomposition on samples 1 and 2. Sample 1, (■) dehydrogenation (k_1), (□) dehydration (k_2); sample 2, (●) dehydrogenation (k_1), (○) dehydration (k_2).

While preliminary experiments with Mn_2O_3 showed that some slight reduction of the catalyst surface took place when it was exposed to isopropyl alcohol at 161°C, no such observation was made at the lower temperatures, 35 to 85°C. In this range the oxide possessed measurable catalytic activity for dehydrogenation but none for dehydration. The dependence of the rate constant for dehydrogenation on temperature is plotted in Fig. 3 for this catalyst and these data yield an apparent activation energy of 15 ± 1 kcal mole^{-1}.

DISCUSSION

Partial reduction of freshly prepared Mn_2O_3 takes place initially at temperatures above 160°C when the oxide is exposed to isopropyl alcohol vapor. These reactions involve the permanent removal of surface oxygen species which take part in an oxidative breakdown of the alcohol to products including carbon dioxide, hydrogen and water vapor, Fig. 1. Although catalysis may occur simultaneously in this initial period, clearly it would be difficult to separate the contributions made by the two sources of reaction to the rates. Hence studies of the simultaneous catalytic dehydration and dehydrogenation of isopropyl alcohol on an oxide with manganese in the

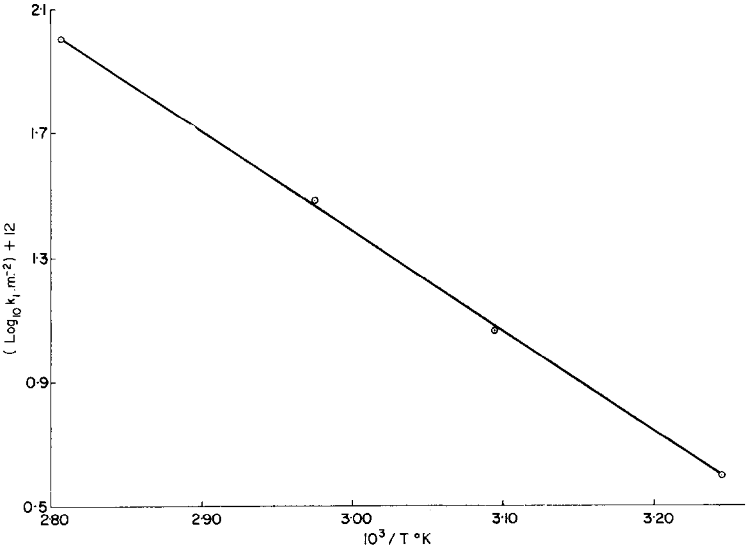

FIG. 3. Arrhenius plot for isopropyl alcohol dehydrogenation on Mn_2O_3.

+3 oxidation state can be carried out only for a range of nonstoichiometric compositions where the metal is present also in the +2 state.

Considering the low value of the partial pressure of water vapor found in the experiments at 161°C, 0.03 mm, it is reasonable to assume that this product is formed by reaction which results in a modification of the manganese(III) oxide composition within the surface of the material. This deduction agrees with the results of X-ray and chemical analyses which showed the absence of other phases in the bulk material. At higher temperatures, reaction leads to the ultimate formation of catalysts with more complex phase structures. Thus, at 207°C the bulk analyses showed clearly that Mn_3O_4 was formed. For all of these reasons earlier results that have been reported (*2*) for catalysis on manganese(III) oxide should be treated with caution.

Table 2 records results obtained with the various catalysts for steady conditions. The apparent activation energies for dehydration increase from 50 to 56 ± 2 kcal mole^{-1} as the oxygen content of the catalysts rises and this trend is climaxed by the complete absence of dehydration activity recorded for Mn_2O_3. The increase may simply reflect greater stability of the dehydration intermediate brought on by an increase in the tenacity with which the hydroxylated dehydration centers (*10*) are held by the surface as the lattice anion deficiency increases from MnO to Mn_3O_4 (*11*).

In MnO, the Mn^{2+} ions occupy octahedral positions (*11*) while Mn_3O_4 has a deformed spinel structure, Mn Mn_2O_4, with a unit cell containing 8 Mn^{2+} ions in tetrahedral configuration and 16 Mn^{3+} ions octahedrally coordinated (*11*). The increase in the presence of octahedrally coordinated Mn ions in the +3 oxidation state is accompanied by a decrease in r_2 and an increase in selectivity towards dehydrogenation. These effects are similar to those reported earlier for ethyl alcohol decomposition on aluminas and alumina–spinel oxides (*10*) where dehydrogenation was favored on catalysts with Al^{3+} ions present in octahedral as opposed to tetrahedral coordination.

Two kinetic regions have been established for the dehydrogenation reaction which are distinguishable by the values of the apparent activation energies. It is convenient to describe these as "high" and "low"-temperature regions although the exact values of temperature vary with the composition of the catalyst. Thus for samples 1 and 2 the apparent activation energy is 27 to 28 ± 1 kcal mole^{-1} between

280 and 220°C and 5 to 8 ± 1 kcal mole^{-1} between 200 and 170°C while for sample 4 (Mn_3O_4) the high value of 26 ± 1 kcal mole^{-1} lies from 210 to 190°C and the low of 8 ± 1 kcal mole^{-1} occurs between 175 and 150°C. Such results may be explained by differences in the rate-controlling step in the two temperature regions or by a variation in the energy of interaction between adsorbate molecules and adsorption sites (*12*). The possibility of attributing the phenomena to a major conductivity transition of the oxide (*13*) can probably be discounted at these temperatures since intrinsic conductivity in MnO would not be expected to commence until temperatures around 500 to 800°C (*14*, *15*). However a change in surface conductivity type may occur similar to that which has been suggested to explain results obtained for the decomposition of isopropyl alcohol on chromia at 400°C (*16*).

In Fig. 4, the logarithm of the rate of dehydrogenation of the alcohol at 175 and 250°C is plotted against the oxygen: manganese ratio of the oxides examined. The reciprocal of the binding energy of the manganese–oxygen bond is included also as an ordinate in the figure. The energies were calculated from published heats of formation data (*17*). Binding energy is defined (*18*) as the standard enthalpy, $\Delta H^0{}_{25°C}$, of the reaction:

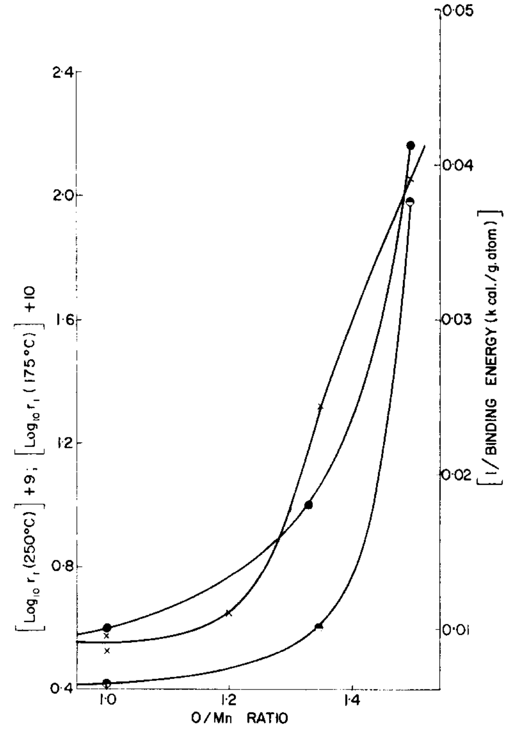

FIG. 4. Log$_{10}$ (rate of dehydrogenation) and (1/binding energy) versus O/Mn ratio. (●) (1/binding energy); (×) rate of hydrogenation at 250°C; ◓ rate of dehydrogenation at 175°C.

$$\frac{1}{m} Mn_xO_y + \frac{1}{2} O_2 \rightarrow \frac{1}{m} Mn_xO_{y+m}.$$

The figure shows a correlation between log$_{10}$ (rate of dehydrogenation) and the reciprocal of the binding energy of the last gram atom of oxygen added to the metal oxide. Earlier (*19*) a similar relationship was established between the selectivity for oxidation of methyl alcohol to formaldehyde on transition metal oxides with similar binding energy values. Also for the oxidation of methane, carbon monoxide, hydrogen and propylene on transition metal oxides it has been shown (*20*) that the rate of reaction increases with decrease in the binding energy, which is a similar result to Fig. 4 since dehydrogenation may be regarded as a redox-type reaction.

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