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Supported Barium Chromate—A New Oxidation Catalyst

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Supported barium chromate has been shown to behave as a vapor-phase oxidation catalyst at temperatures over 200° (*1*). A gamma alumina support with surface area of 80–120 m^2/g is preferable to other supports. Oxidation of isobutane, isobutene, and *n*-butane to carbon dioxide was studied in the temperature range of 200°–400° and E_a values of 10.3, 11.7, and 12.3 kcal/mole determined, respectively. In the catalytic oxidation of aromatic structures small yields of partial oxidation products could be isolated using a catalyst consisting of barium chromate on a support with 0.1 m^2/g surface area. Barium chromate on alumina possesses excellent thermal properties and can be used at temperatures up to 800° with little loss in activity. The catalytic activity of the supported barium chromate is dependent on formation of lattice defects which equilibrate with oxygen to re-establish the original state. Other oxidizing agents such as potassium permanganate and barium ferrate when deposited on a gamma-alumina support were not active for vapor-phase oxidation of hydrocarbons.

INTRODUCTION

Use of chromates, dichromates, and chromic acid as oxidizing agents is well known in the literature and they find many applications as in the preparation of anthraquinone, benzoic acid, saccharin, etc. In these processes the hexavalent chromium is irreversibly reduced to a lower valent state. It is surprising that no known attempts have been made to utilize hexavalent chromium compounds in the form of supported catalysts to carry out vapor-phase oxidation reactions. The high thermal stability of alkali and alkaline earth chromates might be particularly interesting in the current search for oxidation catalysts for use in the oxidation of hydrocarbons in the temperature range of 300–800°C.

In other areas such as olefin polymerization Field and Feller (*2*) have reported that higher valent chromium oxides on alumina can act as catalysts for the low-pressure polymerization of ethylene. The nature of this catalyst has been clarified more recently by Russian workers (*3*) who have concluded that the active species in the catalyst is pentavalent chromium. Another reported use for chromic acid or dichromates as catalysts relates to the decomposition of hydrogen peroxide (*4*) in aqueous media. In this case the dichromate reacts with hydrogen peroxide to form a perchromate which decomposes to oxygen and more dichromate.

Barium chromate was selected for use in the supported catalyst because of its high thermal stability (1100°C) and low solubility in water (3 ppm). Generally, alkali and alkaline earth chromates possess excellent thermal stability, while the dichromates and chromic acid decompose at temperatures of 200–600°. Chromates of the weaker bases Cu, Zn, etc. are reported to lose oxygen at temperatures not greatly different than dichromates (*5*). The low solubility of barium chromate makes it preferable to the other alkali and alkaline earth chromates which are soluble.

This paper is concerned with the preparation and evaluation of supported barium chromate catalyst. Data are presented as to: (1) the effect of various supports, (2) the catalytic oxidation of various hydrocarbons, and (3) the thermal stability of the catalyst. The nature of the catalyst is also discussed.

EXPERIMENTAL

Catalyst Preparation

A. $BaCrO_4$ on Al_2O_3 was prepared by dissolving 15 g of $BaCrO_4$ in 300 ml of boiling

0.9 *M* HNO_3. The concentration of HNO_3 was critical, concentrations higher than 0.9 *M* leading to precipitation of $Ba(NO_3)_2$. After cooling to 25° and filtering, the saturated $BaCrO_4$ solution was poured over 30 g of predried, γ-Al_2O_3, 3 mm cylindrical pellets (Harshaw Al-0104 T) and allowed to stand for 6 hr. The impregnated pellets were filtered, washed with water, dried at 110° and fired 16 hr at 550° in air. Analysis: Ba, 1.94%; Cr, 0.73% (3.7% $BaCrO_4$). The surface area was 94 m^2/g. The same method was used to prepare barium chromate catalysts on silica and alumina-silica supports.

B. $KMnO_4$ was impregnated onto 60 g of γ-Al_2O_3 pellets by immersing the pellets for 16 hr in a solution composed of 48 g of $KMnO_4$ and 600 ml of water from which MnO_2 had been removed by filtration. After filtering and washing quickly with water, the pellets were dried in a desiccator in the dark. The catalyst analyzed for 2.1% $KMnO_4$ and had a surface area of 84 m^2/g.

C. $BaFeO_4$ on Al_2O_3 was prepared by immersing 30 g of -40 $+80$ mesh γ-Al_2O_3 powder in 125 ml of a strongly basic K_2FeO_4 solution prepared according to the procedure of Schreyer, Thompson, and Ockerman (*6*). After 2 hr the K_2FeO_4 solution was decanted and 100 ml of saturated $Ba(OH)_2$ solution was added to precipitate $BaFeO_4$ on the support. The finely divided catalyst stood in the $Ba(OH)_2$ solution about 2 hr after which the K_2FeO_4-$Ba(OH)_2$ treatment was repeated. After impregnation, the catalyst was washed three times with water and dried in a desiccator. Analysis: 0.7% $BaFeO_4$. The surface area of this catalyst was 76 m^2/g.

Equipment and Analytical Methods

Isobutene, isobutane, and *n*-butane oxidation experiments were carried out in a vertical 30-mm OD tubular Vycor reactor heated with two Multiple Unit combustion furnaces. Temperatures in the initial (preheater) portion of the reactor were controlled by a Brown "Pyr-O-Vane" controller while the temperature of the catalyst bed, located 15 cm from the end of the reactor, was controlled by a West Instrument Corp. proportioning program controller. Actual catalyst temperatures were measured with a chromel-alumel thermocouple extending into the center of the bed.

Naphthalene oxidation experiments were made in the same type of reactor except that an electrically heated sidearm located between the preheater and reactor furnaces was included to admit the naphthalene-air feed stream. The naphthalene-saturated air stream was obtained by passing a portion of the air stream upward through a tube containing a fritted glass disc supporting the naphthalene charge. The tube was immersed in a thermostated oil bath. At the exit end of the reactor was located a cold trap maintained at $-75°$ by a dry-ice–acetone bath.

Effluent gases were analyzed using a Perkin-Elmer model 154D vapor fractometer equipped with a printing integrator. A 2 m diisodecyl phthalate on diatomaceous earth column in series with a di-2-ethylhexyl sebacate on silica gel column was used to analyze oxidation products of isobutane, *n*-butane, and naphthalene. Oxidation products of isobutene were analyzed using two 2-m dimethylsulfolane on diatomaceous earth columns operated in series. Thermistor detectors were used with a helium carrier gas flowing at 40 cc/min. The absence of carbon monoxide as an oxidation product was established using a 2-m molecular sieve gas-chromatograph column.

Solid products from naphthalene oxidation were analyzed for naphthalene and naphthoquinone by an ultraviolet spectrophotometric method (*7*) and for phthalic anhydride by base titration.

All surface areas were measured by nitrogen adsorption at $-195°$.

Procedure

A. Rising temperature experiments. A 10.0-g catalyst sample was placed in the reactor and activated 16 hr at 550° in an air stream after which it was cooled to the desired initial temperature. The hydrocarbon was premixed with dry, CO_2-free air so that the feed gas contained 0.1% to 0.5% hydrocarbon. The gas mixture was preheated in the initial portion of the reactor before passing over the heated catalyst bed, the temperature of which was programmed to increase 60°/hr. The effluent gas was analyzed for CO_2, unoxidized hydrocarbon and air at 25° temperature intervals.

B. Isothermal experiments. These experiments were carried out as described above except that the catalyst was cooled to the desired temperature and maintained at that temperature. Analyses were carried out on the effluent gases with the feed stream flowing at eight different rates from 200 to 2000 cc/min. This procedure was repeated for seven different temperatures.

C. Naphthalene oxidation. Twenty grams of catalyst consisting of 5.0% $BaCrO_4$ on Carborundum Company AMC alumina-silica support of surface area 0.1 m^2/g was placed in the reactor. Eight grams of naphthalene was placed in the naphthalene evaporator and heated above the melting point to 110°. A dry, CO_2-free air stream was split, the primary stream passing through the naphthalene evaporator and then into the reactor via the sidearm which was heated to 180°. On entering the reactor, the primary stream was met by the secondary air stream just as it emerged from the preheater. The combined gas stream passed downward over the catalyst bed before entering the cold trap where condensable products were removed. The product analysis based on the amount of naphthalene fed to the reactor was: naphthoquinone, 0.55%; phthalic anhydride, 0.30%; unconverted naphthalene, 23.0%; with the balance of the carbon being accounted for by the CO_2 formed.

Thermal Stability of Supported BaCrO₄ Catalyst

A 30-g sample of catalyst with a surface area of 90 m^2/g was placed in the reactor and maintained in a flowing 0.5% isobutane-air atmosphere at constant temperature for an extended period of time. Temperatures and times used were 600° for 168 hr followed by 700° for 48 hr and finally 800° for 24 hr. After each temperature exposure surface areas were measured and a rising temperature isobutane oxidation run was performed. After 600° exposure, the surface area was 84 m^2/g, while after 800° exposure it had dropped to 68 m^2/g.

An unimpregnated γ-Al_2O_3 support underwent a decrease in surface area from 93 m^2/g to 69 m^2/g when heated at 600° for 168 hr.

Valence of Chromium in BaCrO₄ Catalyst

The average chromium valence was determined for a supported $BaCrO_4$ catalyst which was exposed to an isobutane-air stream at nine temperatures between 180° and 480°. One-gram samples of $BaCrO_4$ catalyst were introduced into the reactor maintained at constant temperature through which a 0.2% isobutane-air stream was flowing. The catalyst remained in contact with the stream for 1 hr after the catalyst had reached the temperature of the reactor. The catalyst was then cooled in a stream of argon. Per cent Cr^{6+} was determined by an iodometric method as adapted by Weller and Voltz (*8*), and then compared with the per cent Cr^{6+} originally present in the catalyst to obtain the following average chromium valences:

Temp. (°C)	180°	245°	275°	305°	315°	345°	395°	445°	480°
Valence	5.8	5.5	5.5	5.2	5.3	5.4	5.5	5.6	5.8

A second method for average chromium valence determination was used in which 1-g samples were analyzed for Cr^{6+} after being withdrawn from a 20-g portion of catalyst during a rising temperature run. Good agreement was obtained at the different temperatures between average chromium valences calculated from this data and the data obtained when the catalyst was cooled in argon before titrating.

RESULTS

The supported barium chromate catalyst was prepared by dissolving barium chromate in an aqueous solution of a strong mineral acid. The support was impregnated with this solution, and then filtered and dried. Activation of the partially dried catalyst was carried out in a rapidly moving air stream between 450° and 550°. The yellow color of the catalyst indicated that a chromate and not a dichromate was present on the support despite the fact that the catalyst was impregnated from acid solution. The low solubility of the barium chromate on the support was further evidence as to the absence of any dichromate. X-ray analysis confirmed the presence of barium chromate on the support as opposed to a mixture of barium and chromium oxides. The concentration of barium chromate on the support could be controlled by varying the concentration of the impregnating solution and the volume of solution per unit weight of support.

The activity of barium chromate on alumina (surface area 94 m^2/g) for hydrocarbon oxidation was determined over a range of temperatures and flow rates using isobutane. As can be seen in Fig. 1, complete oxidation of isobutane to carbon dioxide is obtained in the temperature range of 350–450° for space velocities of 2200, 4600, and 7200 hr^{-1}. Presence of partial oxidation products such as carbon monoxide, aldehydes, or acids could not be detected in the effluent gas. Even at temperatures where per cent conversion was low, only isobutane and carbon dioxide were found in the effluent. Possibly, partially oxidized intermediates are present in the activated state where they would be susceptible to oxidation before they left the catalyst surface.

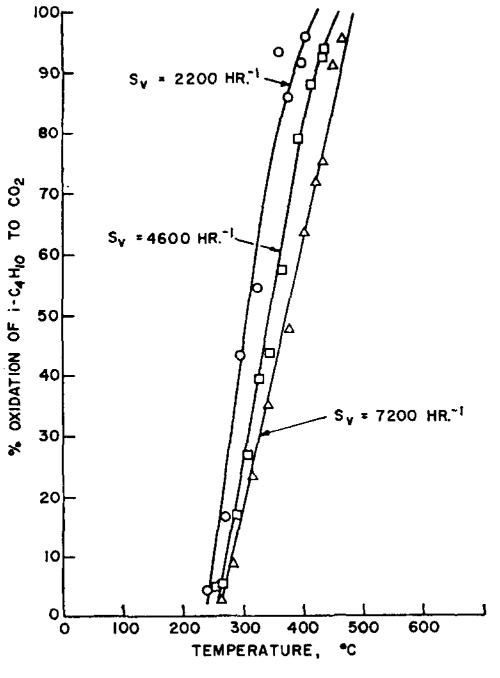

FIG. 1. Influence of space velocity on i-C_4H_{10} oxidation over 12% $BaCrO_4$ on γ-Al_2O_3.

Titration of the catalyst before and after the oxidation of isobutane showed that no reduction of the hexavalent chromium had occurred when the catalyst was cooled in air. In fact, over 99% of the chromium was retained in the hexavalent state when the catalyst was heated in the presence of hydrocarbon and air at 800° for 24 hr and then cooled to room temperature in air. Isolated cases where some reduction took place could generally be explained on the basis of improper impregnation resulting in a catalyst in which the Ba/Cr ratio was less than one. If the catalyst was cooled in an inert atmosphere some reduction could be observed in the hexavalent chromium.

Influence of the support. The effect of various supports on the activity of the barium chromate catalyst was evaluated. In Fig. 2 are shown results of oxidation studies with silica-alumina and alumina supports with surface areas ranging from 80–240 m^2/g. It appears that those systems with surface areas of 80–140 m^2/g are somewhat more active than those with surface areas of 240 m^2/g. This difference in activity may be associated with diffusion-controlling properties of the support and has been noted by other workers in catalytic oxidation of hydrocarbons (*9*). In the absence of a support, barium chromate with a surface area of 3.7 m^2/g possessed a very low activity (approaching that of the unimpregnated support). A physical mixture of 4% of this barium chromate with gamma alumina (surface area 90 m^2/g) yielded an activity somewhat lower than that of the pure barium chromate and almost as low as the unimpregnated support. This tends to indicate that the alumina support in such a physical mixture acts primarily as a diluent for the catalyst and does not participate as a cocatalyst in the oxidation reaction. Efforts to prepare barium chromate with a surface area of about 100 m^2/g were unsuccessful so

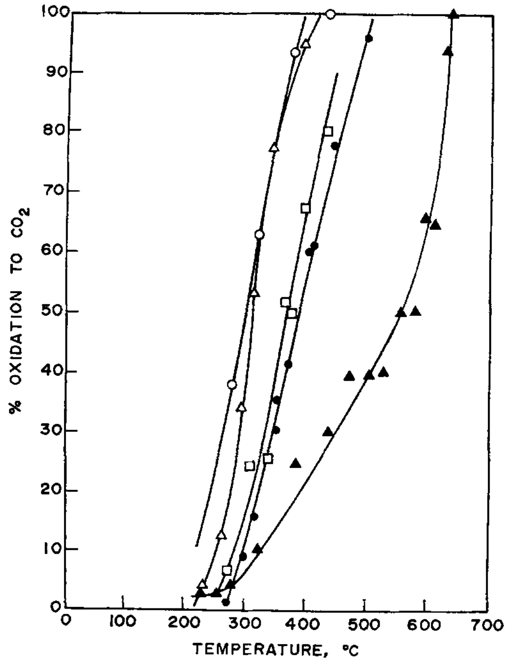

FIG. 2. Oxidation of i-C_4H_{10} over $BaCrO_4$: 3.7% on 80 m^2/g γ-Al_2O_3, ○; 17.0% on 132 m^2/g Al_2O_3-SiO_2, △; 3.3% on 238 m^2/g γ-Al_2O_3, □; 21.9% on 233 m^2/g γ-Al_2O_3, ●; 3.7 m^2/g pure $BaCrO_4$ powder, ▲. All $S_v = 3000\ hr^{-1}$ except pure $BaCrO_4$, $4700\ hr^{-1}$.

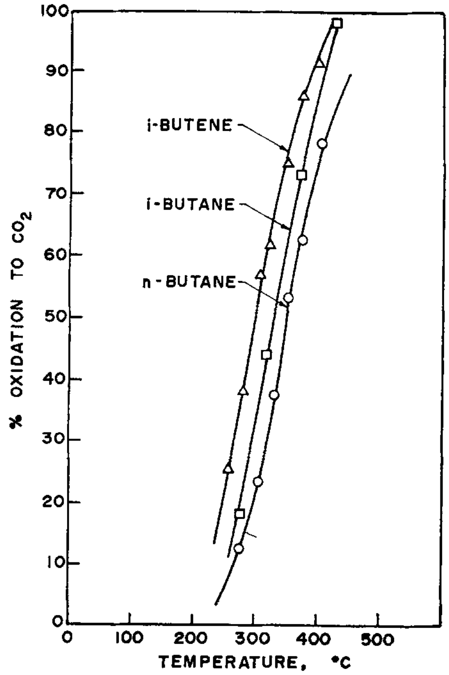

FIG. 3. Influence of hydrocarbon structure on oxidation. All $S_v = 5000\ hr^{-1}$.

that this point could not be conclusively proven. Variations in concentration of barium chromate on alumina over a range of 1–20% did not appear to affect the activity of the catalyst appreciably.

Other work with alumina and silica supports showed that the silica at higher temperatures became less active. On this basis the gamma-alumina support with surface area of 90 m^2/g was selected for subsequent studies.

Effect of hydrocarbon structure. Oxidation of isobutane, isobutene, and *n*-butane were studied to determine the effect of structure of hydrocarbon on the activity of the catalyst. It was found, as shown in Fig. 3, that the barium chromate on alumina for the same temperature was more active with isobutene than with isobutane which in turn was more easily oxidized than *n*-butane. This sequence would be expected since olefins are more easily oxidized than saturated hydrocarbons and branched hydrocarbons more easily than straight-chain hydrocarbons. However, it should be noted that the differences in activity were slight and that the barium chromate catalyst is not particularly sensitive to structural variations in hydrocarbons.

In all these cases rates of oxidation were measured under isothermal conditions and apparent activation energies calculated using a variation of Bridges and Houghton's (*10*) method. Plots of log W/F vs. $1/T$ where W = g of catalyst and F = mole of hydrocarbon in the feed per hour, were constructed at constant conversion in the range from 30% to 70% conversion. From the slopes of the straight lines obtained, apparent activation energies were calculated. Values for E_a of 12.3, 10.3, and 11.7 kcal/mole were obtained in the oxidation of *n*-butane, isobutane, and isobutene, respectively. The close agreement among the three values indicates that the mechanism for the oxidation of these hydrocarbons is identical. This work was carried out with a 3.7% barium chromate on alumina catalyst.

The relationship of W/F to space velocity (Sv), enables one to calculate a temperature vs. per cent conversion curve at constant Sv from a W/F vs. conversion plot.

$$Sv = \text{STP flow}/V_c = \frac{(2.24 \times 10^4)(100\%)(D_c)}{(W/F)(\% \text{ Hydrocarbon in feed})}$$

where D_c is catalyst density and V_c is catalyst volume. Agreement between temperature vs. per cent conversion curves calculated in this manner and those obtained at the same space velocity from rising temperature experiments is excellent.

With aromatic structures such as benzene and naphthalene, the barium chromate on alumina was too active, yielding carbon dioxide as the only oxidation product. Preliminary experiments using supports with surface areas in the range of 0.1–2 m²/g were carried out. With this type of catalyst, small yields of naphthoquinone and phthalic anhydride were observed in the oxidation of naphthalene.

Thermal stability of supported $BaCrO_4$. A study of the thermal stability of a barium chromate catalyst in the temperature range of 600–800° showed that the alumina support was stabilized by the barium chromate. This is in contrast to the reported (*11*) detrimental effect of other metal oxides to the stability of alumina supports. Thus, heating the unimpregnated support at 600° for 168 hr resulted in a 25% loss in surface area. The supported catalyst on the other hand showed a 6% loss in surface area under similar treatment.

The catalyst suffered only a slight loss in activity from this thermal treatment (see Fig. 4). On heating at 700° for 48 hr a more noticeable drop in activity was observed, and 25–35° higher temperatures were required to achieve the same degree of oxidation. An additional heating cycle at 800° for 24 hr did not reduce the activity of the catalyst any further. A 20% loss in surface area was noted in the catalyst after the entire thermal cycling.

Discussion

Nature of the $BaCrO_4$-Al_2O_3 catalyst. The activity of the supported barium chromate catalyst in hydrocarbon oxidation is undoubtedly associated with the formation of small amounts of lower valent states of chromium resulting in lattice defects. These defects are very mobile, particularly once catalytic temperatures are reached. Thus, chemisorption of oxygen at the surface of the catalyst would tend to regenerate the hexavalent chromium, while the oxidation of the hydrocarbon would result in an oxygen-deficient structure containing new defects.

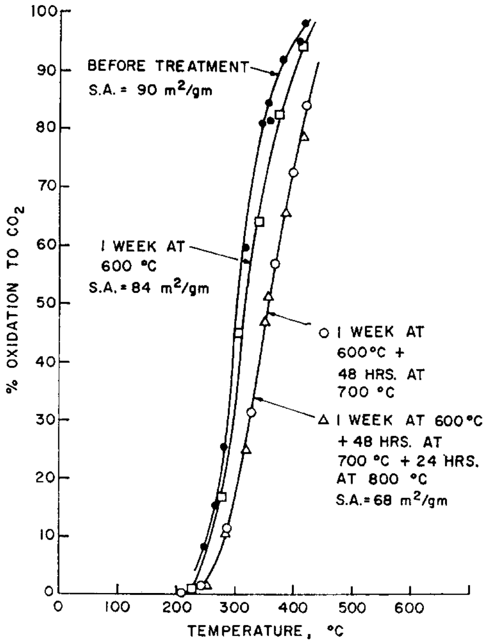

Fig. 4. Thermal stability of 12% $BaCrO_4$ on γ-Al_2O_3.

This was tested experimentally by studying the composition of the supported barium chromate catalyst during the oxidation of isobutane. Normally on cooling the catalyst in air after an oxidation experiment, the chromium is completely in the hexavalent state. It was, therefore, necessary to cool the catalyst in argon in order to determine the average valence state of the chromium during the hydrocarbon oxidation. It was found that at 395° an average valence of 5.5 existed, while at a higher temperature of 480° the valence was 5.8. At lower temperatures of 275° and 345°, valences of 5.5

and 5.4 were observed. From these results it appears that the catalyst in actual use consists of a mixture of Cr^{6+} and lower valent states of chromium. The ease with which the catalyst completely converts to Cr^{6+} on cooling in air suggests that the lower valent state is Cr^{5+}.

The variation in average valence at different temperatures, ranging from 5.2 up to 5.80, indicates that in the lower range, Cr^{6+} behaves as a lattice imperfection in Cr^{5+} while in the higher range, Cr^{5+} represents a defect structure of Cr^{6+}. Possibly, both conditions exist simultaneously on the surface of the catalyst and neither effect can be isolated. This would be consistent with the observed results in which no break in activity can be observed with change in average valence.

Simard *et al.* (*12*) have investigated the composition of a vanadium pentoxide catalyst during the oxidation of *o*-xylene and observed a similar mixture of valence states in the active catalyst. They concluded from their study that V_2O_5 and $V_2O_{4.34}$ were the active constituents. This can also be interpreted as an equilibrium between V^{5+} and V^{4+} in the catalyst (*13*) which results in the lattice defects necessary for catalytic activity.

In comparing available data on the chromate and vanadium pentoxide it appears that the chromate is not only a stronger oxidizing agent than vanadium pentoxide (*14*), but is also a much stronger catalyst for oxidation of hydrocarbons.

It seemed worthwhile, therefore, to explore the possibility that oxidizing agents stronger than chromate (such as $KMnO_4$ and $BaFeO_4$) might provide even stronger oxidation catalysts for hydrocarbons. [There is a report (*15*) in the literature that silver permanganate is an active catalyst for oxidation of carbon monoxide to carbon dioxide.] Potassium permanganate and barium ferrate were deposited on alumina supports and activated in an air stream at temperatures just below 180° and 250°, respectively. The supported permanganate decomposes irreversibly at 180° while the supported ferrate decomposes at 270°. This can easily be observed in the color change from violet to brown and violet-red to brown for the two respective systems. Since the products of decomposition in both cases are active catalysts for oxidation of hydrocarbon, catalytic activity was investigated only up to the decomposition temperatures. It was found that both systems were inactive for isobutane oxidation up to their decomposition point. On the other hand, supported barium chromate does show catalytic activity at temperatures as low as 230–250° which is well below the decomposition point for barium ferrate. Therefore, although both permanganate and ferrate are considerably stronger oxidizing agents than the chromates, neither system appears to act as an oxidation catalyst for hydrocarbons. This indicates that under the conditions of catalytic oxidation the permanganate or ferrate do not form defect structures which can rapidly equilibrate with oxygen to reestablish the higher valent forms.

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