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The Oxidation of Hydrocarbons and CO Over Metal Oxides

II. α-Cr_2O_3

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Four types of α-Cr_2O_3 microcrystals with different morphological appearances were prepared and used as the catalysts for the oxidation of C_2H_4, C_3H_6, C_2H_6, C_3H_8, and CO. The reaction rate per unit area as a function of temperature (200-450°C) and the partial pressures of O_2, hydrocarbon or CO, CO_2, and H_2O were determined using an on-line continuous inlet mass spectrometer. The catalytic selectivity and the reaction kinetic parameters were found to be dependent on the morphological structure of the catalyst surface. The kinetic data also suggested that, at high concentrations, O_2 and hydrocarbon molecules were competing for the same sites. Neither the hydrocarbons nor CO would react with the surface lattice oxygen at the reaction temperatures.

When two hydrocarbons (or CO and a hydrocarbon) coexisted in the reaction mixture, mutual retardation was observed in all the combinations. Kinetic isotopic effects for the oxidation reactions were determined using C_2D_4, C_2D_6, and CD_3CHCH_2. The results showed that C–H bond breaking was involved in the rate-controlling step in the C_2H_6 oxidation, but not in the case of C_2H_4. Adsorption results showed that only a very small fraction of the surface was catalytically active. These findings are very similar to those obtained over the NiO surface.

INTRODUCTION

It was the purpose of this work to obtain the kinetic and some mechanism data for the complete oxidation of simple hydrocarbons and CO over some well-defined metal oxide catalysts using as wide a range of controlled reaction conditions as possible. In the first part of this series, the results over NiO crystals have been reported (*1*). In this report, similar studies have been extended to α-Cr_2O_3 crystals to examine the dependency of the kinetic parameters on the nature of the metal oxide catalyst. It was found that the rate of C_2H_4 oxidation over NiO crystals was slightly dependent on the crystalline faces exposed. Such dependence of the catalytic activity on the surface structure has been theoretically predicted [see, for example (*2*)] but experimentally little evidence has been reported on nonmetal catalysts. This effect has been ignored in the previous studies of hydrocarbon oxidation over metal oxides as most of the catalysts did not have well-defined surfaces in a geometrical sense. α-Cr_2O_3 has been chosen for this study since it affords a possible way of investigating the geometrical effect. α-Cr_2O_3 can be prepared either in the form of very thin platelets exposing predominantly the (001) face or as well-defined polyhedrons exposing several crystalline faces. For the experiments described below, the oxidation reactions have been carried out over four morphologically different α-Cr_2O_3 crystals.

EXPERIMENTAL METHODS

The Catalyst Preparations

The Cr_2O_3 catalysts used for this study were prepared as follows:

Cr_2O_3 (JM) was the Spec pure grade Cr_2O_3 powder purchased from Johnson-

Matthey Co. Ltd. The manufacturer's reported concentration of the impurities Fe, Si, Na, Cu, and Mg are all less than 5 ppm. The powders were composed of randomly shaped crystals exposing an undetermined number of crystalline faces.

Cr_2O_3 (KB) were crystals prepared by flux growth method using Cr_2O_3 (JM) as the starting material and anhydrous $K_2B_4O_7$ (B&A reagent grade) as flux. The mixture was heated in a platinum crucible at 1300°C for 16 hr and cooled down to 900°C in about 30 min. The crystals obtained were washed repeatedly with hot diluted HNO_3 and distilled water. To eliminate the possible surface contamination by Pt from the crucible, the crystals were reheated at 900°C in a quartz container for 3 days and then washed with hot aqua regia, followed by repeated diluted HNO_3 and water washing. The crystals both before and after the aqua regia washing and the aqua regia wash solution itself were analyzed for Pt by activation analysis. The total Pt found in the crystals was less than 30 ppm, and was less than 6 ppm in the crystals treated with aqua regia (limits of detection). Other impurities found in the crystals were K and B at about 20 ppm each. The X-ray diffraction pattern identified the crystals as α-Cr_2O_3. Electron micrographs of the crystals (Fig. 1a) showed well-defined polyhedral crystals with several undetermined crystalline faces exposed.

Cr_2O_3 (Si) was prepared by thermal decomposition of $K_2Cr_2O_7$ (B&A reagent grade) in a quartz crucible at 900°C and washed repeatedly with diluted HNO_3 and H_2O. The crystals were reheated at 900°C for 24 hr and washed with HF to get rid of any contamination of Si. The crystals were very thin platelets with distinctive hexagonal appearance as shown in Fig. 1b. x-Ray identified the flat surface of the platelets which constituted over 90% of the total surface as the (001) face of α-Cr_2O_3. Another crystal Cr_2O_3 (A) was prepared using the same procedures but in a gold crucible. The crystals obtained were both morphologically and catalytically similar to that of Cr_2O_3 (Si). Therefore, to avoid repetition, the results over Cr_2O_3 (A) are not reported separately. The use of a Pt crucible is to be avoided when decomposing $K_2Cr_2O_7$ to Cr_2O_3 because it results in severe (3%) Pt contamination of the Cr_2O_3.

Cr_2O_3 (Si-G) was prepared by crushing Cr_2O_3 (Si) in an agate mortar and pestle, washed with hot HF followed by diluted HNO_3 and H_2O. It was sintered at 850°C to constant area before being used as catalyst.

The surface area of the catalysts was determined by Kr adsorption at $-195°C$ and calculated using BET equation. The results are listed in Table 1. The surface areas remained unchanged in all cases after having undergone up to 30 catalytic oxidation–heating cycles.

The Reactors and Reagents

The reactors and gases used were the same as that reported previously (*1*).

The Determination of the Oxidation Rates

The compositions of the ambient gases both before and after passing over the catalyst were determined using a continuous inlet CEC 614 mass spectrometer. The procedures adopted have been described previously (*1*) with the exception that a Teflon tube was used between the reactor and the mass spectrometer to minimize the loss of H_2O through adsorption on the walls of the connecting tubes. The correspondence in the change of the water peak with those of CO_2 and the reactants was so good that the water formed could be quantitatively measured in this study.

The same pretreatment for the catalyst surface as that used for NiO was adopted. That is, the catalyst surface was cleaned

TABLE 1
SURFACE AREA OF THE CATATYSTS

Catalyst	Surface area (m^2/g)
Cr_2O_3 (JM)	1.31
Cr_2O_3 (KB)	0.15
Cr_2O_3 (Si)	1.96
Cr_2O_3 (Si-G)	1.64

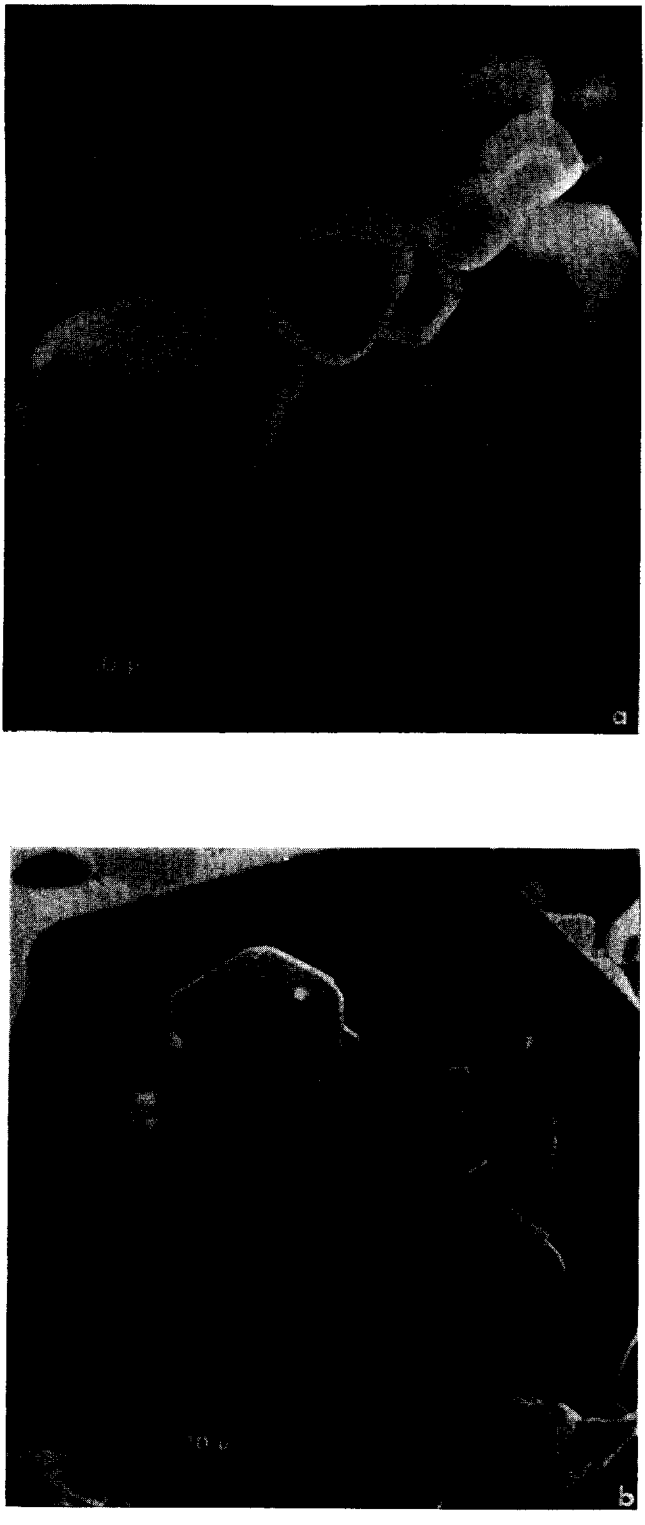

FIG. 1a. Cr_2O_3 (KB); (b) Cr_2O_3 (Si).

by heating in a flowing N_2 or He stream containing a few percent of O_2 at 800–900°C prior to the first oxidation run of each catalyst and at 500–600°C in between successive runs. The activity of the catalyst in a series of runs was checked from time to time with the oxidation of C_2H_4 under a standard set of conditions. Neither the activity nor the surface area changed significantly after a series of 5 to 35 runs.

For the kinetic studies, the percentage of conversion was kept below 10% of the minor component in most cases, except where high activity at low partial pressure of one of the reactants occurred. For the stoichiometric studies, conversions as high as 30–40% have been reached to ensure the accuracy.

RESULTS AND DISCUSSION

The General Behavior of the Reactions

As it was found previously over the NiO catalysts (*1*), the rate of oxidation over Cr_2O_3 catalysts was slightly inhibited by the presence of water but independent of the partial pressure of CO_2. Therefore, for the oxidation of the hydrocarbons, sufficient water was added in the inlet gas to minimize the variation of the partial pressure of water across the catalyst bed. In the case of CO oxidation, a liquid nitrogen trap was placed in the inlet line to remove moisture in the gas stream. With the partial pressure of H_2O maintained within a narrow range, the absolute specific reaction rate at very low conversions was found to be independent of the total flow rate at a fixed ambient composition, suggesting that the reactions were not controlled by the transport of the gas phase.

The reactions were conducted at such low conversion and the surface areas of the catalysts were so small that significant heating due to the heat of the reaction is not expected. This is also confirmed by the fact that the rates were independent of the flow rate and that the Arrhenius plots were the same irrespective of the reaction sequence, heating, or cooling.

In many of the reactions reported here, the formation of CO_2 and H_2O went through an initially high rate, then decreased with time to a relatively stable value. The response of the reaction rate to the subsequent change of ambient composition was almost instantaneous. The percentages of rate decrease from the initial rates to the stabilized rates are designated as "self-deactivation" and are reported in the last column of Table 2. It should be noted that these values should be somewhat dependent on the gaseous compositions and the reaction temperatures used. The single values quoted are intended to show qualitatively in which reactant–catalyst systems such a phenomenon was observed. Furthermore, for the oxidation of the olefins over Cr_2O_3 (Si) where a large initial self-deactivation effect was observed, a slow increase or decrease of reaction rate was found for subsequent large changes in the gaseous composition during the course of the run. This differed from that observed over NiO, where the decrease of rate with time at near-constant reaction conditions was irreversible and appeared only at the beginning of each run.

The Stoichiometry of the Reactions

The ratios of O_2, hydrocarbon (or CO) consumed, and CO_2 and H_2O produced over the various Cr_2O_3 catalysts are listed in Table 2. The consistently higher than theoretical value for O_2 consumed, which was also found for the complete combustion of C_2H_4 at 550°C, but not for the oxidation of CO, may be attributed to the change of the mass spectrometer sensitivity for O_2 in the presence of hydrocarbon. The slightly higher value for water relative to CO_2 may also result from the same uncertainty in the sensitivity calibration. For these reasons, small differences from stoichiometry will be ignored in the consideration of the results.

Over Cr_2O_3 (JM) and Cr_2O_3 (KB), the hydrocarbons were stoichiometrically converted to CO_2 and H_2O. There was little self-deactivation taking place in these cases, whereas over Cr_2O_3 (Si) only part of the C_2H_4 and C_3H_6 was recovered as CO_2 and H_2O. The reactions were also accompanied by a high degree of self-

TABLE 2
STOICHIOMETRY OF THE REACTIONS AT 300°C

Catalyst	Hydrocarbon	O_2 :	HC (or CO) :	CO_2 :	H_2O	Self-deactivation (%)
Cr_2O_3 (JM)	C_2H_4	3.6	1	2.1	2.1	0
	C_3H_6	5.1	1	3.1	3.1	0
	C_2H_6	4.5	1	2	3	0
	C_3H_8	6.5	1	3.7	4.6	0
	CO	0.5	1	0.95		10
Cr_2O_3 (KB)	C_2H_4	3.6	1	2	2.1	5
	C_3H_6	5.5	1	3	3.1	4
	C_2H_6	4.2	1	2.1	3.1	0
	C_3H_8	6	1	2.8	4	0
	CO	0.55	1	1		5
Cr_2O_3 (Si)	C_2H_4	3.3	1	1.6	2	40
		(3.9	1	2.1	2.2)	
	C_3H_6 (0.5%)	3	1	1.4	1.8	70
		(4.6	1	2.2	2.8)	
	C_3H_6 (0.06%)	4.3	1	2.4	2.9	20
	C_2H_6	4.2	1	2	3.1	5
	C_3H_8	5.9	1	3.5	4.2	50
	CO	0.5	1	0.86		25
Cr_2O_3 (Si-G)	C_2H_4	3.5	1	2.1	2.2	30
	C_3H_6	5.2	1	3.2	3.3	40
	C_2H_6	4.1	1	1.9	2.9	5
	CO	0.5	1	0.9		15

deactivation. An intermediate situation prevailed over the Cr_2O_3 (Si-G) catalyst. Over Cr_2O_3 (Si) the amount of hydrocarbon not recovered as CO_2 and H_2O decreased with increasing reaction temperature, or decreasing partial pressure of the hydrocarbon, or increasing reaction time, or a combination of these conditions. Searching through the mass spectra, no compound other than the reactants and CO_2 and H_2O was found. Heating the catalyst at 500–600°C after each run with nitrogen or helium containing a few percent O_2 could produce only a very small amount of CO_2 (0.01–0.02 ml CO_2/m^2) and regenerated the catalytic activity completely. This implies that a major portion of the hydrocarbon missed was converted into some material of low volatility and retained in the cold section of the connecting tubes. Only a very small fraction was retained on the surface and perhaps caused the self-deactivation effect. This result would indicate that the (001) face of α-Cr_2O_3 should be useful in producing partially oxidized products.

For the oxidation of CO, the ratios of O_2, CO, and CO_2 were near stoichiometric over all the Cr_2O_3 catalysts. However, some self-deactivation was observed. This suggests that a small fraction of the oxidation product or intermediate was retained on the surface, causing loss of activity. But in contrast with the hydrocarbon oxidation, no gross loss of CO was observed.

For C_2H_6 oxidation, the ratios were near stoichiometric, and no self-deactivation was observed.

The Reaction Kinetics

Hydrocarbon oxidation. Typical results on the specific rate of CO_2 formation as a function of partial pressure of O_2 or hydrocarbon while the partial pressure of the other reactant and H_2O were maintained within ±5% are shown in Figs. 2–5 for the four catalysts. Only results at 300°C are included, although experiments have

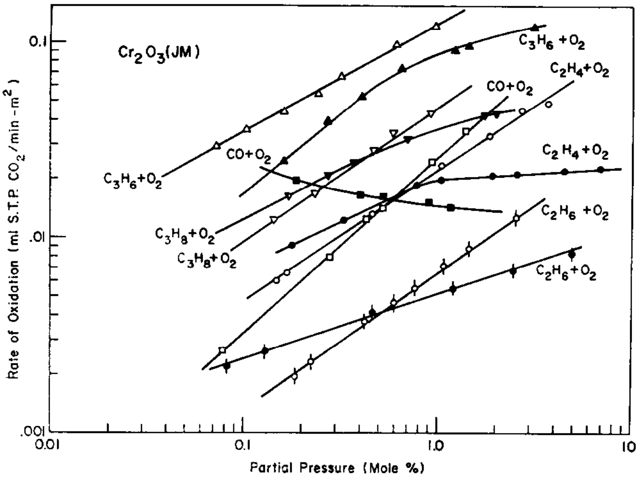

FIG. 2. Rate of oxidation over Cr_2O_3 (JM) at 300°C, 0.3% H_2O for hydrocarbons and 0% H_2O for CO. Pp's kept constant during the runs are: (○) 1.9% O_2; (●) 0.9% C_2H_4; (△) 1.7% O_2; (▲) 0.6% C_3H_6; (ϕ) 1.2% O_2; (●⃒) 0.76% C_2H_6; (▽) 1.9% O_2; (▼) 0.9% C_3H_8; (□) 1.2% O_2; (■) 0.45% CO.

been conducted at each 25–50°C interval within the range of 250–400°C for each hydrocarbon/catalyst combination. The general features of the rate curves are relatively independent of the reaction temperature, except the data over Cr_2O_3 (Si), which is described below. The effect of partial pressure of H_2O was also determined at constant partial pressure of O_2 and hydrocarbon and was found to be usually of the order of −0.2 to −0.3; i.e., slightly inhibiting the reaction. Addition of CO_2 into the inlet gas had no effect on the reaction rates.

In each of these log–log plots, there is a linear portion covering a relatively large range of partial pressure variations; but changes of the slopes and/or maxima and minima are found in many cases as the ranges of the partial pressures increase. Thus, one can obtain a partial reaction order with respect to either reacting component varying from a positive fractional order to zero and sometimes to a negative

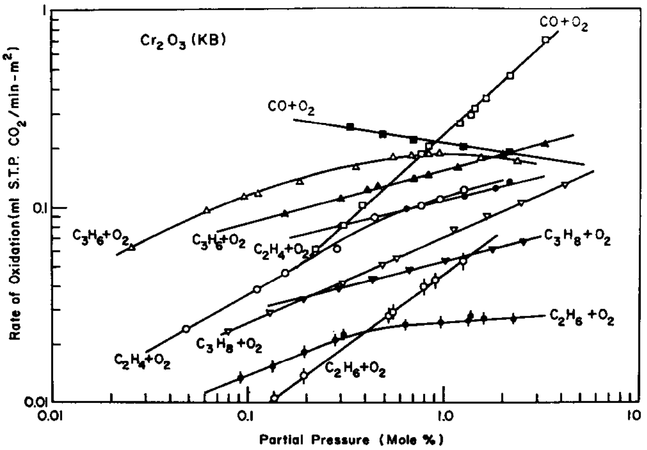

FIG. 3. Rate of oxidation over Cr_2O_3 (KB) at 300°C, 0.3% H_2O for hydrocarbons and 0% H_2O for CO. Pp's kept constant during the runs are: (○) 1.1% O_2; (●) 0.95% C_2H_4; (△) 1.45% O_2; (▲) 0.55% C_3H_6; (ϕ) 1.4% O_2; (●⃒) 0.5% C_2H_6; (▽) 1.1% O_2; (▼) 0.6% C_3H_8; (□) 1.2% O_2; (■) 0.76% CO.

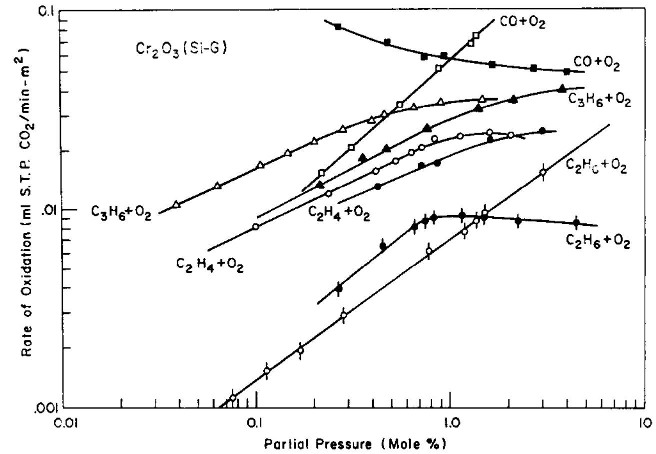

FIG. 4. Rate of oxidation over Cr_2O_3(Si-G) at 300°C, 0.3% H_2O for hydrocarbons, 0% H_2O for CO. Pp's kept constant during the runs are: (○) 2.0% O_2; (●) 1.1% C_2H_4; (△) 1.6% O_2; (▲) 0.9% C_3H_6; (ϕ) 1.6% O_2; (♦) 1.3% C_2H_6; (□) 2.7% O_2; (■) 0.88% CO.

fractional order, depending on the ambient conditions used. This may account for some of the discrepancies in reaction orders reported in the literature (*3*). The decreasing reaction order with respect to component A, while partial pressure of B is held constant, signifies the saturation of adsorption of A on the catalytically active sites.

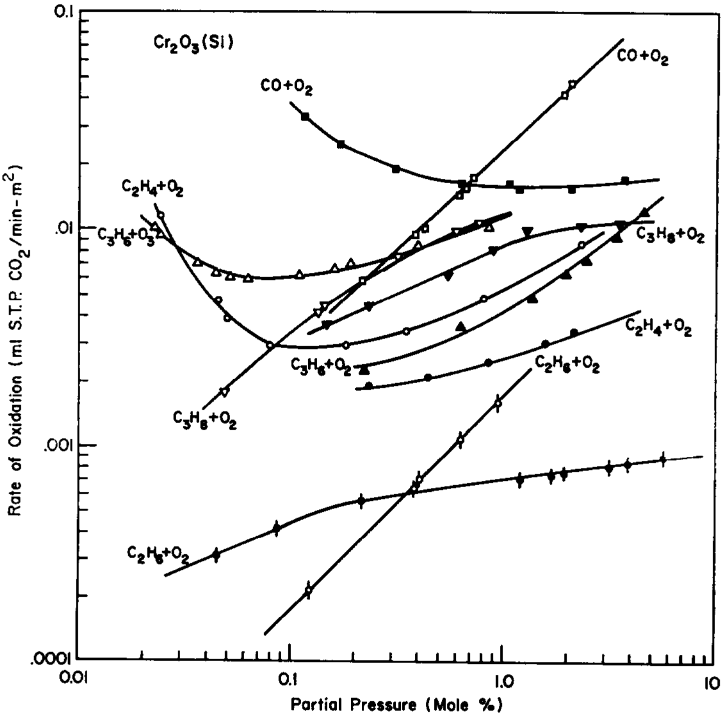

FIG. 5. Rate of oxidation over Cr_2O_3(Si) at 300°C, 0.3% H_2O for hydrocarbons, 0% H_2O for CO. Pp's kept constant during the runs are: (○) 2.1% O_2; (●) 0.36% C_2H_4; (△) 4% O_2; (▲) 0.8% C_3H_6; (ϕ) 1.2% O_2; (♦) 0.4% C_2H_6; (▽) 1.3% O_2; (▼) 0.6% C_3H_8; (□) 1.2% O_2; (■) 0.65% CO.

The appearance of maximum is expected in the cases where A and B are competing for the same sites, and the reaction follows Langmuir-Henshelwood type mechanism. It has been reported that hydrocarbons are preferentially adsorbed on the surface cations (*4*). O_2 would certainly prefer the positively charged surface Cr ions rather than the O^{2-} sites. Therefore, the surface Cr ions are the most likely candidates for the active sites. It is interesting to note that for the olefins over Cr_2O_3 (JM) the maxima or changes of slope in the rate curves were observed for varying partial pressure of O_2 but not for varying partial pressure of hydrocarbon within the range shown in Figs. 2 and 4, whereas for the olefins over Cr_2O_3 (KB) the reverse is true. Such differences among the catalysts probably reflect the relative strength of adsorption of O_2 and hydrocarbons over the various surfaces rather than a change of the reaction mechanism.

For the oxidation of the two olefins over Cr_2O_3 (Si), broad minima were observed as a function of the partial pressure of the olefins. The occurrence and the position of the minimum were dependent on the ambient composition, the reaction temperature, and the sequence of the reaction experiments. Increasing reaction temperature or starting the reaction at high partial pressures of O_2 and very low partial pressure of hydrocarbon and moving toward higher partial pressure of hydrocarbon, or both, could produce a rate curve with a maximum instead of a minimum. The rate of CO_2 formation over this catalyst was also less than those over the other three catalysts. These findings together with the severe self-deactivation and nonstoichiometric conversion found over Cr_2O_3 (Si) suggest that some side reaction, in addition to complete oxidation, also takes place over the Cr_2O_3 (Si) catalyst. This may not be surprising, since several reactions, such as partial oxidation to aldehydes and acids, dehydrogenation, polymerization, and cyclization have been reported to take place for hydrocarbon over Cr_2O_3 catalysts [see, for example (*5*)]. The present results suggest that the relative rates of such reactions are influenced by the crystalline faces exposed.

The oxidation kinetics of C_2H_6 and C_3H_8 are quite similar over the four catalysts, as contrasted to the different kinetics shown over the four catalysts by olefins, suggesting that reaction mechanism for the oxidation of the saturated and unsaturated hydrocarbons may be different. Further evidence for this contention will be presented later.

For the purpose of comparison, the specific rates of the reactions at 300°C under the conditions of 1% O_2, 0.1% hydrocarbon or CO (also 1% CO), and 0.3% H_2O (0% H_2O for CO) over all four catalysts are listed in Table 3. The apparent activation energies are also included in the last column. These oxidizing conditions are taken because they are in the range that self-deactivation is less and also they are within the range of the automobile exhaust composition. It is shown that the rates of oxidation of the olefins are greater than their corresponding paraffins, and the larger molecules oxidize faster than the smaller ones in the homolog, except for Cr_2O_3 (Si), over which the olefins were not completely converted to CO_2 and H_2O. CO oxidizes at a rate of the same order of magnitude as the hydrocarbons, but the rate increases faster with increasing partial pressure of CO. Such dependence of rates on molecular structure of the hydrocarbons suggests that O_2 adsorption is not the rate-determining step for the complete oxidation.

The rates are highest over the polyhedral Cr_2O_3 (KB) and lowest over the Cr_2O_3 (Si) platelets with Cr_2O_3 (JM) and Cr_2O_3 (Si-G) (both of random-shaped crystals) of intermediate values. In view of the fact that Cr_2O_3 (KB) was prepared from Cr_2O_3 (JM) and Cr_2O_3 (Si-G) from Cr_2O_3 (Si), such differences in the rates and in their kinetic parameters can only be attributed to their morphological differences.

CO oxidation. The results for the oxidation of CO over the four catalysts are included in Figs. 2–5 and Tables 2 and 3. In contrast to the oxidation of the hydrocarbons, the partial pressure dependence for

TABLE 3
THE RATE OF OXIDATION

Catalyst	Hydrocarbon	Rate[a] (ml STP/min-m_s)	ΔE (kcal/mole)
Cr_2O_3 (JM)	C_2H_4	0.0045	21.5
	C_3H_6	0.030	24.1
	C_2H_6	0.0013	21.0
	C_3H_8	0.0087	24.7
	CO	0.0034 (0.027[b])	15.3
Cr_2O_3 (KB)	C_2H_4	0.035	22.2
	C_3H_6	0.104	26.6
	C_2H_6	0.0080	21.3
	C_3H_8	0.024	27.5
	CO	0.031 (0.24[b])	11.8
Cr_2O_3 (Si-G)	C_2H_4	0.0065	
	C_3H_6	0.014	
	C_2H_6	0.0014	
	CO	0.0085 (0.064[b])	
Cr_2O_3 (Si)	C_2H_4	0.0022	
	C_3H_6	0.0035	
	C_2H_6	0.0002	
	C_3H_8	0.0036	
	CO	0.0027 (0.024[b])	

[a] Rate at 1% O_2, 0.1% hydrocarbon or CO, 0.3% H_2O (0% H_2O for CO).
[b] Rate at 1% O_2, 1% CO, 0% H_2O.

the CO oxidation is about the same over the various catalysts: negative fractional to zero order with respect to partial pressure of O_2. Addition of CO_2 to the inlet gas stream had no effect on the rate, while H_2O at low concentration (less than $\sim$0.5%) could reduce the rate slightly. At high partial pressure of H_2O (>1%), the reaction rate increased momentarily, and then decreased to a value showing net inhibition. In general, the CO was stoichiometrically converted to CO_2 with some self-deactivation. Pretreating the surface with CO at the reaction temperature in the absence of O_2 could increase the subsequent CO + O_2 reaction rate significantly, but the increased activity would gradually disappear with time. Pretreating the surface with O_2 could increase the activity only slightly. Thus, the self-poisoning effect could not be attributed to the oxidation or reduction of the surface, rather some reaction intermediate or by-product formed from CO and O_2 reaction adsorbed on the surface.

The specific rates for CO oxidation at the standard conditions as shown in Table 3 were similar to that for the hydrocarbons and decreased in the order of Cr_2O_3 (KB) > Cr_2O_3 (Si-G) > Cr_2O_3 (JM) $\geq$ Cr_2O_3 (Si). At the same partial pressures the rates over each of the four catalysts showed a general trend of $C_3H_6 > C_3H_8 >$ CO $\simeq C_2H_4 > C_2H_6$. This differed from that observed over NiO, for which CO oxidation was faster than all the hydrocarbons studied.

In view of the fact that rates for CO and hydrocarbon oxidation over Pt surface were reported (*3*) to be several orders of magnitude greater than that found over the Cr_2O_3 catalysts, one might suspect that the high activity over Cr_2O_3 (KB) could be derived from small amount of Pt transferred from the crucible used during flux growth, even though special precaution of washing with hot aqua regia and careful analysis of the sample for Pt had been made. Such Pt contamination effect can be excluded, based on the following. A study of the oxidation of CO and the hydrocarbons over several noble metals including Pt has been made by the author (*6*). The results showed that, over Pt, the oxidation rates for C_2H_4 and C_3H_6 were 1.5–2.0 order with respect to oxygen and −1 order with respect to the hydrocarbons. For CO, the reaction orders were 1.2 for O_2 and −0.5 for CO. Only part of the olefins reacted was recovered as CO_2. Under the standard conditions of Table 3, the specific rates for CO/Pt were 50–100 times those of olefins/Pt. These kinetic parameters are so distinctively different from those obtained over Cr_2O_3 (KB) that any significant contribution of Pt contamination on Cr_2O_3 (KB) can be ruled out.

Competitive Oxidation Reactions

The competitive oxidation of four pairs of gases over Cr_2O_3 (JM) is shown in Table 4. The R_A and R_B are the rates of component A and B in the mixed gas and $(R_A)_0$ and $(R_B)_0$ are the respective rate for each gas if alone and under the otherwise same conditions. It is shown that mutual retardation occurred in all cases, but not to the same degree for the two components. The predominance order of $C_3H_6 > CO \simeq C_2H_4 > C_2H_6$ is the same as that obtained over NiO (*1*) and several other metal oxides by Moro-oka and Ozaki (*3*). This retardation effect coud be interpreted as competition for O_2 adsorbed or as competition for adsorption sites among the hydrocarbons. It is difficult to decide which is operative, based on the present results alone.

TABLE 4
COMPETITIVE OXIDATION OVER Cr_2O_3 (JM) AT 300°C

Hydrocarbon (%)			
A	B	$R_A/(R_A)_0$	$R_B/(R_B)_0$
C_2H_4 (0.5)	C_3H_6 (0.3)	0.40	0.90
C_2H_4 (1.2)	C_2H_6 (1)	0.95	0.20
CO (1)	C_3H_6 (1)	0.40	0.80
CO (1)	C_2H_6 (1.2)	1	0.25

Kinetic Isotopic Effect

For further exploring the reaction mechanism, the oxidation rates for three deuterated hydrocarbons, C_2D_4, C_2D_6, and CD_3CHCH_2, were determined over Cr_2O_3 (JM). The results are shown in Table 5. They are very similar to those obtained over the NiO crystals (*1*) and lead to the following conjecture: Ethane with its isotopic effect of 0.45 undergoes C–H bond breaking and adsorption on the surface as ethyl radicals as the rate-controlling step. While C_2H_4 with isotopic effect of 1 is most likely adsorbed on the surface through the double bond with the rate of adsorption or with subsequent attack at this bond being the rate-limiting step. In the case of C_3H_6, the isotopic effect of 0.76 at 300°C is intermediate of the other two and suggests that the concerting processes of allyl hydrogen splitting and adsorption through a smeared-out double bond (so-called allyl complex) prevails. This is in agreement with the low C–H bond energy for the allyl hydrogen in the propylene molecule (83 vs 98 kcal for that in ethane, and 103 kcal for that in ethylene).

TABLE 5
KINETIC ISOTOPIC EFFECT OVER Cr_2O_3 (JM)

Hydrocarbons	k_D/k_H	T (°C)
C_2D_4 vs C_2H_4	1	(300)
CD_3CHCH_2 vs C_3H_6	0.76	(300)
	0.88	(350)
C_2D_6 vs C_2H_6	0.45	(300)

Adsorption of O_2, CO, and Hydrocarbons Over Cr_2O_3 (Si)

The adsorption of O_2 was measured using a conventional constant volume adsorption apparatus. On a surface outgassed at 450°C, then exposed to 2 mm Hg of O_2 at 300°C, only about 0.01 ml STP O_2/m^2 was adsorbed within the first minute. Some slow uptake following an Elovich-type equation was also observed. This is in agreement with that reported by Weller and Voltz (*7*). CO_2 adsorption over a O_2 presorbed surface is of the order of 0.004 ml/m^2. Admitting C_3H_6 (0.1%) to the O_2 presorbed surface at 300°C would give about 0.012 ml CO_2/m^2 and about 0.006 ml/m^2 additional C_3H_6 was retained by the surface. Over a surface outgassed at 450°C and no O_2 presorbed, the amount of C_3H_6

adsorbed is 0.01 ml/m^2. At 300°C, 0.5% CO in helium would react with an O_2 pretreated surface to give 0.013 ml CO_2/m^2. Readmitting 1.5% O_2 to the CO presorbed surface gave 0.1 to 0.3 ml CO_2/m^2. These results show that neither CO nor C_3H_6 would react with the surface lattice oxygen. The adsorption sites for O_2, or hydrocarbon or CO, constitute a very small fraction of the surface. Therefore, the catalytic sites for the oxidation reactions would be an even smaller fraction of the Cr_2O_3 surface.

Effect of Other Added Compounds

In addition to H_2O and CO_2, several other compounds which are possible gas phase reaction intermediates or reaction poisons were injected into the reacting gas to examine their effect on the reaction rates for C_3H_6 oxidation over Cr_2O_3 (Si).

1. CH_3COOH and CH_3CHO. The presence of either of these compounds in small quantity could temporarily suppress the oxidation of C_3H_6. The suppression was completely reversible, and no permanent change of the rates after complete removal of these compounds was observed. The oxidation rate of the aldehyde or the acid to CO_2 in the presence of C_3H_6 was much less than if either of them were alone. In contrast to that found over NiO, the oxidation rates over Cr_2O_3 (Si) for CH_3CHO and CH_3COOH in the absence of C_3H_6 were of the same order of magnitude as that of C_3H_6. At high concentration ($>0.1\%$ of p_{CH_3COOH}), the rate of oxidation of CH_3COOH to CO_2 was found to be self-inhibiting. Therefore, neither of these compounds appears to be a candidate for possible reaction intermediates leading to CO_2 formation. Since it has been reported that acrolein is oxidized to CO_2 at a lower rate than CH_3CHO (*8*), the possibility of C_3H_6 to CO_2 via $CH_2{=}CHCHO$ is also unlikely. If such aldehydes and acids were the product of the side reaction, then their high volatility would give distinctive peaks in the spectra; and this was not the case.

2. SO_2. SO_2 was injected into the reacting stream of $O_2 + C_3H_6 +$ He in small doses; the reaction rate decreased progressively with increasing amount of SO_2 added. At near monolayer coverage, the rate had dropped to about 20% of the original value. This is quite similar to that found over NiO and indicates that SO_2 does not selectively adsorb on the catalytically active sites. However, the SO_2 over Cr_2O_3 is easier to be removed from the surface than that over NiO. Heating to 800°C in a few percent O_2 in He can restore over 70% of the activity lost.

3. NH_3. NH_3 was found to reversibly suppress the C_3H_6 oxidation while it was itself being converted to N_2O at a relatively slow rate. In the absence of C_3H_6, NH_3 was converted into NO and N_2O over the Cr_2O_3 (Si) catalyst. C_3H_6 appeared to suppress the NO formation more severely than for the N_2O formation.

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