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The Oxidation of Hydrocarbons and CO Over Metal Oxides

I. NiO Crystals

YUNG-FANG YU YAO AND J. T. KUMMER

Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121

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The catalytic oxidation of CO, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8-1, *trans*-C_4H_8-2 and *i*-C_4H_8 at 200–400°C have been studied using NiO microcrystals exposing predominantly their (111) face as the catalyst. The composition of the gaseous phase was continuously analyzed using an on-line mass spectrometer. The specific reaction rate could be expressed by the empirical power law:

$$\text{rate of CO}_2\text{ produced} = kp_{O_2}{}^m p_{HC}{}^n / p_{H_2O}{}^l,$$

with $0 < l,\ m,\ n < 1$. The apparent activation energies of the reactions were 24–25 kcal/mole for the alkenes and CO and 17 and 21 kcal/mole for C_2H_6 and C_3H_8, respectively. A change of ΔE to lower values at temperatures less than 270°C was also observed in a few cases. The rates of hydrocarbon (HC) converted to CO_2 per unit area increased only slightly with increasing chain length of the hydrocarbons. The reaction kinetic parameters over the (111) face were compared with those over randomly oriented polycrystalline powders and the geometrical effect was found to be small.

The following aspects of the reactions have also been studied: (1) the adsorption of O_2, C_3H_6, H_2O and CO_2, together or separately on the catalyst surface, (2) the competitive oxidation between pairs of coexisting hydrocarbons, (3) the kinetic isotopic effect for C_2D_6/C_2H_6, C_2D_4/C_2H_4 and CD_3CHCH_2/C_3H_6, (4) the rate of oxidation and the effect on hydrocarbon oxidation of several possible reaction intermediates, CH_3CHO, CH_3COOH and ethylene oxide and (5) the effect of possible reaction poisons, SO_2 and HCl. Based on the results obtained, some information on the reaction mechanism was derived.

INTRODUCTION

The complete oxidation of hydrocarbons and CO to CO_2 and H_2O is of prime importance in automotive emission control. Heterogeneous catalytic oxidation using some metal oxide offers one of the promising means to attain this goal. For these applications, the kinetic parameters of the reaction at ambient conditions approaching that prevailing in the automobile exhaust and some information on the reaction mechanism are needed. However, such data are rather scarce in the literature. This may be attributed to the following causes: The reaction is highly exothermic and the kinetic data can only be obtained at well-controlled conditions. In most of the work reported (*1–4*), the catalysts used were either supported catalysts with unknown surface distribution of the active components or powders after varying degrees of thermal activation. The reactions were often conducted at a limited set of initial ambient conditions and carried out to high conversion. Such conditions are unsuitable for evaluating the kinetic parameters.

It was the purpose of this work to study the complete oxidation of a few simple hydrocarbons and CO over some well-defined metal oxide catalysts. This paper concerns the use of NiO crystals exposing predominantly their (111) face as the catalyst. The ambient conditions have been varied over as wide a range as possible. The effects on the reaction rate produced by the nature of the reactants, the physical and chemical nature of the catalyst surface, the presence of externally added components and the competitive oxidation among hydrocarbons have also been examined.

EXPERIMENTAL METHODS

The Catalyst Preparation

The NiO crystals used as the catalyst were prepared using a technique similar to that reported previously (*5*). Equal amounts of NiO powder (Johnson Matthey Co. Ltd., Specpure grade) and anhydrous $Na_2B_4O_7$ (Matheson, Coleman & Bell, reagent grade) were thoroughly mixed and heated in a gold crucible to 960°C for 2 hr. The melt was quenched in air to room temperature and the flux was leached out with hot dilute HNO_3 and distilled H_2O. The leaching and washing procedures were repeated at least 10 times. The crystals thus obtained are designated as NiO(I) and are all octahedrons as shown in the scanning electron micrograph (Fig. 1). Emission spectroscopic and X-ray fluorescence analysis of these crystals showed that no Na or Au was present to the extent of the instrumental limits of 0.001%.

The majority of the catalytic oxidation reactions reported in this communication were performed over these NiO(I) crystals unless stated otherwise. In the process of searching for a proper catalyst, a number of other NiO crystals have also been used in the exploratory work. Some interesting findings together with the catalyst preparations are described separately in a later section.

The surface areas of the catalysts were determined by Kr adsorption at −195°C and calculated using BET equation. The results are included in Table 1. The surface areas remained constant during a series of 20–30 experiments including heating to 800° between successive runs.

The Reactants

Chemical pure or research grade cylinder gases of N_2, He, O_2, C_2H_4, C_3H_6, C_4H_8-1, *trans*-C_4H_8-2, *i*-C_4H_8, C_2H_6, C_3H_8 and CO_2

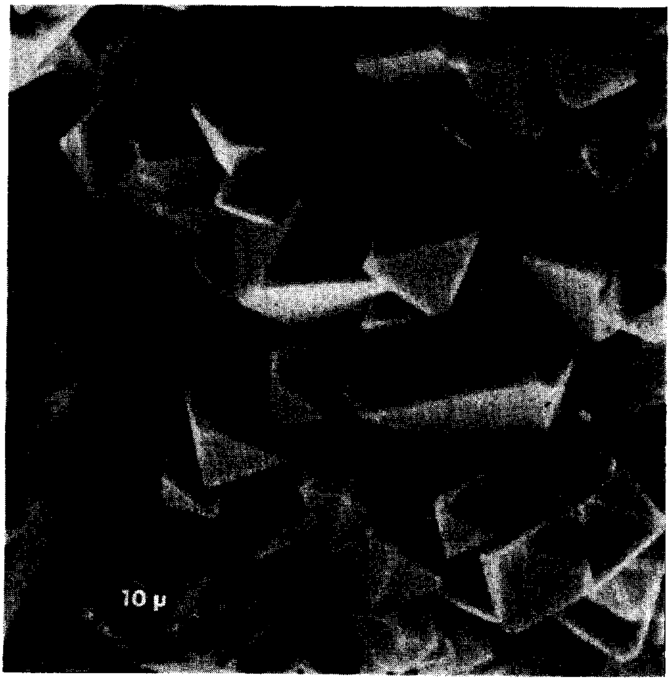

FIG. 1. NiO(I) crystals

TABLE 1
Surface Areas of NiO Catalysts

Catalyst	Descriptions	Surface area (m^2/g)
NiO(I)	Octahedrons, prepared in gold crucible	0.281
NiO(II)	Powders, J. T. Baker Co. Reagent	1.65
NiO(III)	Powders, Johnson-Matthey Specpure	0.30
NiO(IV)	Octahedrons, prepared in Pt crucible	0.233
NiO(IV-W)	NiO(IV) washed with aqua regia	0.233
NiO(IV-C)-1	NiO(IV-W) crushed, 550°C preheating	0.594
NiO(IV-C)-4	NiO(IV-C)-1, 800°C additional preheating	0.363

were used without further purification. C_2D_4 was purchased from Isomet Co. and the on-line determined isotopic purity was about 92%. CD_3CHCH_2 and C_2D_6 were purchased from Merck Co. with claimed isotopic purity of >95%.

The Determination of the Oxidation Rates

The catalyst was held in a cylindrical quartz reactor which was one leg of a U tube, the other leg served as a preheater for the reactants. The catalyst bed depth was 1 to 2 cm and there was very little pressure drop across the bed. The reactor was surrounded with a tube furnace the temperature of which was controlled and recorded to ±0.5°C through a thermocouple placed in a well at a point near the center of the catalyst bed. The carrier gas, He or N_2, and the reactants after being mixed in a mixing chamber were continuously led through the reactor or its bypass and then to a CEC 614 mass spectrometer for continuous on-stream analysis. The gas line was copper tubing with stainless steel valves with no organic material such as grease present. The gas composition could be changed at will by adjusting the metering valve at each source of gas. The total gas flow rate was measured using a soap bubble flowmeter at the exit and the minimum required flow was limited by the inlet flow characteristics of the mass spectrometer of 2.1 ml/min. The sensitivity of the system allowed an evolution of CO_2 of 1×10^{-5} ml/min to be detectable. To correct for CO_2 and H_2O formed on the filament of the mass spectrometer, the background spectrum was recorded for each variation in the inlet gas composition. For the rate function measurements, the percentage of conversion and therefore the pressure differential across the catalyst bed at steady state was kept below 10% of the minor component. Whenever the conversion exceeded 5%, the mean values of the inlet and exit partial pressures instead of the exit values were taken as the partial pressures over the catalyst. For stoichiometric or material balance studies, conversions as high as 30–40% were allowed to improve the accuracy of the results. The complete mass spectra between *m/e* of 12 to 80 both through the reactor and at the bypass were taken to search for any product in addition to CO_2 and H_2O present in the gas phase.

Provisions were also made to inject various compounds such as acetic acid, SO_2, etc., into the inlet gas. Water was introduced into the system either by injection or by passing the carrier gas through a cooled reservoir filled with fused Al_2O_3 presoaked with water.

Adsorption Measurements

A conventional volumetric gas adsorption apparatus with a Decker differential pressure gauge (0–5 mm Hg range) was used for the Kr, O_2, CO_2, H_2O and hydrocarbons adsorption measurements. The catalyst was usually outgassed at 500°C for 2–3 hr to 1×10^{-6} mm Hg prior to each series of adsorption measurements. In a few cases, the gaseous phases were collected in a liquid nitrogen cooled side arm and analyzed using a CEC 103 mass spectrometer.

RESULTS AND DISCUSSION

The Stoichiometry of the Reactions

The amounts of O_2 and hydrocarbon or CO consumed and that of CO_2 formed were determined from the flow rates and the changes in the mass spectrometric peak heights. The ratios are shown in Table 2. The H_2O formed could not be accurately measured due to the adsorption of water on the walls of the copper tubings and the instrument. C_2H_4, C_2H_6, C_3H_8 and CO were found to be completely converted to CO_2 and no extraneous compound was detected in the mass spectra. The slightly higher than theoretical consumption of oxygen found might be attributed to the change in the mass spectrometer calibration factor for O_2 in the O_2–hydrocarbon mixture from that in the air. For C_3H_6, in addition to CO_2 some by-product with mass peaks of 45, 55 and 56 was detected. But the amount of this secondary product was so small that an identification was not possible. For the three butene isomers, up to 25–40% of the butenes were not recovered as CO_2. The spectra showed small increase in m/e of 55 and 43. This could be due to the fact that the ratios of $p_{O_2}/p_{C_4H_8}$ for the stoichiometric determinations were in most cases less than the stoichiometric value of 6, as it was found that the reactions shifted toward complete oxidation with increasing $p_{O_2}/p_{C_4H_8}$ ratio. Prolonged oxidation (over 4–5 hr) could also shift the ratios to near stoichiometric values (see the values in parentheses in Table 2). Because of this complication and because our main interest is the complete oxidation, all the rates in this report are expressed in terms of CO_2 produced per unit area rather than O_2 or hydrocarbon consumed.

TABLE 2
OXIDATION OF HYDROCARBONS (HC) AND CO ON NiO(I)

Reactant	Temp range (°C)	O_2:HC:CO_2 Experimental	O_2:HC:CO_2 Theoretical
C_2H_4	200–400	3.2:1:2	3:1:2
C_3H_6	200–400	4.8:1:2.9	4.5:1:3
C_4H_8-1	300–400	4.9:1:2.6	6:1:4
i-C_4H_8	300–400	4.5:1:2.3 (5.6:1:2.5)	6:1:4
C_2H_6	150–400	4:1:2.2	3.5:1:2
C_3H_8	150–400	8:1:3.8	7:1:3
CO	150–300	1:2:2	1:2:2

To evaluate the possible contribution of surface reduction or participation of lattice oxygen to the overall CO_2 production, the catalyst was also exposed to the carrier gas containing only the hydrocarbon without O_2 at 300–400°C. It was found that under such conditions, the CO_2 produced was negligible and only a very small amount of hydrocarbon, less than 2–3% of a monolayer, was taken up by the catalyst. Such adsorption is discussed further in a section below.

The Kinetic Parameters of the Reactions

In the absence of H_2O added in the inlet gas or preexposure of the catalyst to water vapor, the rate of the reaction went through an initial maximum at about 2–4 min after admitting the reactants followed by a sharp decrease amounting to 20–40% of the maximum and then a slow decrease in rate with time lasted 10–30 min. The height of the maximum was greater for the alkenes and C_3H_8 than for CO and negligible for C_2H_6. It is also strongly dependent on the catalyst pretreatment conditions, for instance, washing with dilute HNO_3 and H_2O followed by heating to 500°C or higher would give a very high maximum while traces of hydrocarbon in the gas phase during the heating treatment would surpress it. The activity lost during these initial decay processes, fast and slow, was irreversible at the reaction temperature. It could be regenerated only by heating in an inert gas stream or a few percent of oxygen to 500°C or higher. Once the stabilized condition had been reached for one hydrocarbon, changing the ambient composition with or without changing the hydrocarbon as reactant would give a new stabilized rate almost instantaneously. Therefore, the initial decrease of activity is due to some cause common to all the hydrocarbon studied. Since the initial fast decay of activity was transient in nature and it was difficult to reproduce quantitatively, it is not considered further in this work.

The slow decrease in activity could be eliminated by carrying out the reaction with H_2O added in the inlet gas or exposing the catalyst to H_2O vapor (0.1–0.5%) prior to the admission of the reacting gas. As shown below, H_2O could inhibit the oxidation and the inhibition was readily reversible at $p_{H_2O} > 0.05\%$ but more slowly at lower p_{H_2O}. Therefore, it is reasonable to assume that the slow decrease of activity in the absence of added H_2O was caused by H_2O made in the reaction or a small amount of water in the inlet gas which was taken up by the catalyst slowly.

The stabilized rate of reaction was generally quite reproducible. However, spurious values of severalfold higher or lower have also been obtained in a few runs. Unusually high activity could be brought on by washing with HNO_3 and H_2O, or repeated evacuation to 1×10^{-6} mm Hg at 500°C or prolonged oxidation of isobutene. However, such high activity would invariably decrease to the same stabilized value after several hours of a hydrocarbon oxidation run. The occasional low activity could be traced to some accidental poisoning. To ensure that the results obtained for various reactant compositions and temperatures were on the same stabilized catalytic activity basis, the catalysts were heated at 800°C in a few percent of oxygen between successive runs to get rid of any oxidizable material left on the surface. The CO_2 evolved during these heat treatments was found to be usually <0.02 ml/m². The stabilized activity of the catalyst was checked with C_2H_4 oxidation at a standard set of conditions for each set of experiments. The results reported in this paper for the most part were obtained under the condition of the same catalyst activity and in a few cases they were converted to the same activity using C_2H_4 oxidation as standard.

The dependence of the rate of reaction, measured by CO_2 produced per unit area, on the partial pressure of O_2, hydrocarbon, CO_2 and H_2O at a particular temperature was determined by varying one partial pressure at a time and keeping the others constant to ±5%. Addition of CO_2 to the inlet gas had no effect on the reaction rate. For the other three components, linear relations were obtained in the log–log plots of

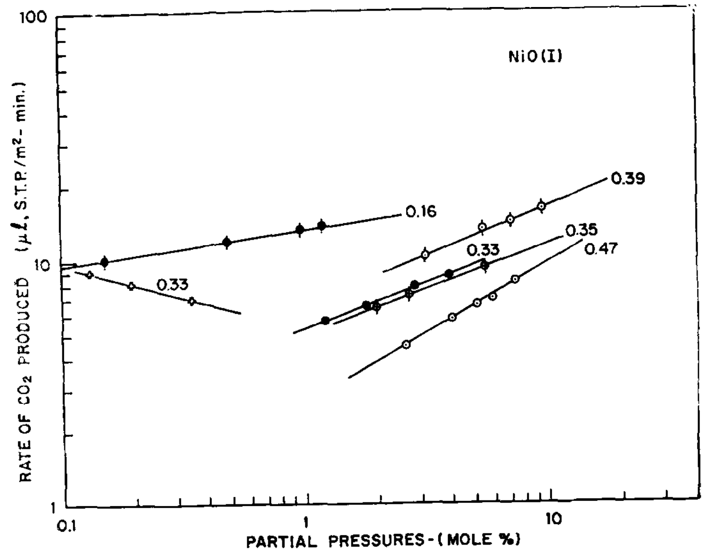

FIG. 2. Oxidation of C_2H_4 over NiO(I). Parameters held constant: (⊙) 317°C, C_2H_4, 2.4%; H_2O, 0.16%; (●) 317°C, O_2, 7%; H_2O, 0.16%; (⊕) 317°C, O_2, 5.5%; H_2O, 0.15%; (✥) 317°C, O_2, 7%; C_2H_4, 4%; (ϕ) 330°C, C_2H_4, 1%, H_2O, 0–0.05% (⧫) 330°C, O_2, 5%, H_2O, 0–0.05%.

rates versus partial pressure of each component. Typical results are shown in Figs. 2 and 3. In Figs. 2–4, the temperatures and partial pressure listed are held constant. The unlisted parameter is varied as indicated by the absissa. The slopes are numbers on the curves. Thus, the oxidation reaction rate expression can be empirically written as:

$$R = kp_{O_2}{}^{m} p_{HC}{}^{n} / p_{H_2O}{}^{l}, \quad (1)$$

where R is the rate (ml STP) of CO_2/m²-min, and p_{O_2}, p_{HC} and p_{H_2O} are the partial pressures (mole %) of O_2, hydrocarbon and H_2O, respectively. The total pressure was 1 atm with the balance the carrier gas, N_2 or He. k is the apparent rate constant. l, m, n are obtained from the slopes of the log–log plots.

In the cases where no H_2O was added to the inlet gas, that is, p_{H_2O} was not constant and was proportional to the CO_2 produced, the reaction rate was found to be dependent on the total flow rate to a positive fractional order as shown in Fig. 4. When the partial pressure of H_2O was kept fairly constant, the specific rate (ml STP) of CO_2 produced/min-m² of catalyst at essentially constant p_{O_2}, p_{HC} (low % of conversion employed) and p_{H_2O} became independent of the flow rate. This absolute specific rate vs flow rate at constant ambient condition relationship should be distinguished from the dependence of percentage of conversion on the space velocity frequently reported in other studies. Such results indicate that the reaction was free of gas phase transport control in the range of the flow rate employed, 5–40 ml/min. Qualitatively, one can visualize that the flow rate effect obtained at no H_2O in the inlet gas can result from the p_{H_2O} effect as the partial pressure of H_2O formed in the reaction is inversely related to the flow rate. One can also estimate that the partial reaction orders of m' and n' obtained under such conditions should be smaller than the corresponding m and n values obtained at near constant p_{H_2O}. Therefore, one should bear this in mind in comparing the kinetic results obtained under different reaction conditions.

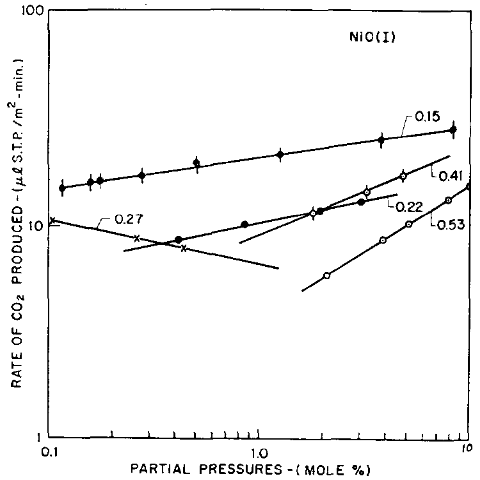

FIG. 3. Oxidation of C_3H_6 over NiO(I). Parameters held constant: (⊙) 317°C, C_3H_6, 0.85%; H_2O, 0.4%, (●) 317°C, O_2, 5.1%; H_2O, 0.4%; (X) 317°C, O_2, 3%; C_3H_6, 0.85%; (ϕ) 330°C, C_3H_6, 0.3%; H_2O, 0–0.2%; (⧫) 330°C, O_2, 5.5%; H_2O, 0–0.2%.

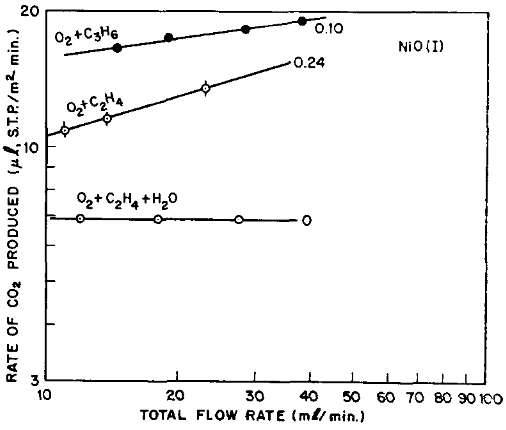

FIG. 4. Effect of flow rate on rate of oxidation over NiO(I). Parameters held constant: (⊙) 317°C, O_2, 7%; C_2H_4, 4%; H_2O, 0.16%; (●) 330°C, O_2, 3%; C_3H_6, 0.28%; H_2O, 0–0.2%; (ϕ) 330°C, O_2, 4%; C_2H_4, 1%; H_2O, 0–0.1%.

The partial reaction orders l, m, n obtained over NiO(I) are shown in Table 3. Each set of these values have been reproduced at least twice at each temperature and at least two temperatures more than 50°C apart for each hydrocarbon or CO. With the exception of C_2H_6, they were found to be independent of the tempera-

TABLE 3
KINETIC PARAMETERS FOR HYDROCARBON OXIDATION OVER NiO(I)[a]

Reactant	l	m	n	ΔE (kcal/mole) (°C)
C_2H_4	0.33	0.47	0.33	25.4 (250–400)
C_3H_6	0.27	0.53	0.23	25.0 (250–400)
C_4H_8-1	0.35	0.55	0.14	24.7 (300–350)
trans-C_4H_8-2	0.33	0.48	0.20	~25 (300–350)
i-C_4H_8	0.35	0.58	0.10	~25 (300–350)
C_2H_6	0.27	0.44	0.50 (350°C)	17.0 (>270)
	—	0.07	0.95 (240°C)	6.8 (<270)
C_3H_8	0.26	0.29	0.53	21.0 (>230)
				~7 (<230)
CO	—	0.47	0.55	25.1 (>220)
				15 (<220)

[a] Temp, 250–400°C; rate of CO_2 produced $= k(p_{O_2})^m p_{HC}^n / p_{H_2O}^l$.

ture. In view of the low sensitivity in the log–log plots and the slight variation in the partial pressures which we attempted to hold constant (up to 5%), the uncertainty in the values of l, m, n could be as large as ±10%. In general, the linearity in the log–log plots was found to be good within the range of the gas compositions used. The partial pressure ranges used were: O_2, 1–20%; C_3H_8 and C_3H_6, 0.05–3%; C_2H_4 and C_2H_6, 0.1–5%; CO, 1–5%; C_3H_8, 0.5–3%; and H_2O, 0.1–1.5%. Combinations of the gases were such that the hydrocarbon (or CO) to O_2 ratio fell within the range of 0.01–2 with most of the experiments carried out in large excess of O_2. The p_{H_2O} was such that the inlet p_{H_2O} was much larger than that produced from the reaction to minimize the differential in p_{H_2O} across the catalyst bed.

The l, m, and n values for the various hydrocarbons over NiO(I) (Table 3) show that H_2O inhibits the reactions to approximately the same degree for various hydrocarbons ($l = 0.25$ to 0.35). The partial reaction order with respect to O_2 is about 0.5, with the exception of C_2H_6 oxidation at <270° in which $m \simeq 0$. There is a slight increase in m with decreasing corresponding value of n. The partial reaction order with respect to hydrocarbon n decreases in the order: $C_3H_8 \simeq C_2H_6 > C_2H_4 > C_3H_6 >$ *trans*-$C_4H_8 > C_4H_8$-1 $>$ *i*-C_4H_8. If the n values can be taken as a measure of the adsorption strength as that found by Moro-oka and Ozaki (*6*, *7*), then the above results are in accordance with the prediction that alkenes are adsorbed stronger than the alkanes and that the larger molecules are adsorbed more strongly than the smaller ones in the homolog. The fractional orders with respect to the two reactants and the reversed trend in the change of m values versus that of the n values could be taken as an indication for the Langmüir-Hinshelwood type mechanism, that is, O_2 and hydrocarbons are competing for the same sites and the reactions between adsorbed O_2 and hydrocarbon at neighboring sites are important. However, as shown below, not all of the evidence supports this contention.

The apparent activation energies of the oxidation reaction on NiO(I) were obtained from the Arrhenius plots. Typical results are shown in Fig. 5 and Table 3. The activation energies were found to be independent of the gas composition. Changes in the slopes of the Arrhenius plots were observed for C_2H_6, CO and C_3H_8 over NiO(I) and for C_2H_4 over another NiO catalyst to be reported later. A change of activation energy for CO oxidation on NiO powder at 250°C has been reported previously and was attributed to the change in the magnetic property of the NiO catalyst (Neel point) (*8–10*). In the present case, the temperatures at which the

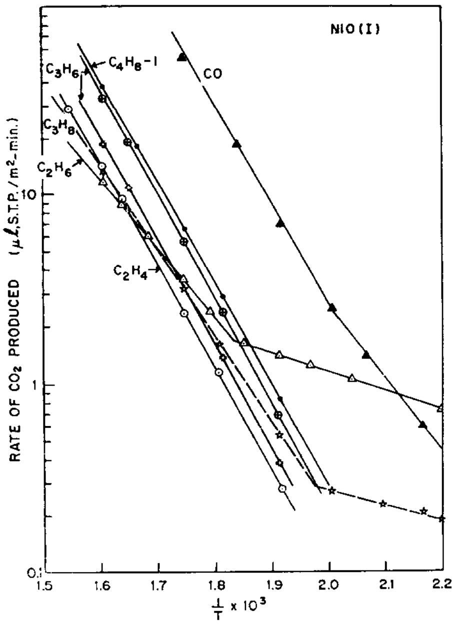

FIG. 5. Arrhenius plots for oxidation over NiO(I): (⊙) C_2H_4, 2.5%; O_2, 6.2%; H_2O, 0.4%; (✚) C_3H_6, 0.8%; O_2, 3.5%; H_2O, 0.4%; (⊕) C_3H_6, 3.2%; O_2, 7%; H_2O, 0.5%; (●) C_4H_8-1, 1.8%; O_2, 5.3%; H_2O, 0.5%; (☆) C_3H_8, 0.4%; O_2, 3.6%; H_2O, 0.3%; (△) C_3H_6, 1.6%; O_2, 2.5%; H_2O, 0.25%; (▲) CO, 2.1%; O_2, 2.7%; H_2O, 0%.

change of slopes occurred are different for different reactants. Therefore, the changes more likely result from a shift in the rate-determining step or reaction mechanism rather than any intrinsic property of the catalyst such as its magnetic property. It is of interest to note that the activation energies for the olefins and CO oxidation are approximately the same at >270°C and they are greater than that of the two alkanes.

For the purpose of comparison, it is desirable to know the rate for each hydrocarbon/catalyst combination at some standard set of reaction conditions. To do this, the average k values of Eq. (1) for each hydrocarbon or CO at several temperatures were computed using a large group of rate data obtained at various ambient conditions and the l, m, n, values listed in Table 3. The rates for each hydrocarbon at 4% O_2, 1% hydrocarbon or CO and 0.1% H_2O were calculated from the k values. The results at 300 and 350°C are shown in Table 4. It is shown that the number of hydrocarbon molecules converted to CO_2 per unit time per unit area increases only slightly with increasing size of the molecule. In terms of the rate of CO_2 produced or O_2 consumed, the increase is proportionally much larger with the size of the molecule. Therefore, it is unlikely that the availability of oxygen is rate controlling. The lack of large dependence for the activation energies and the specific rates on the chain length of the alkenes implies that the rate-limiting step is the same for the C_2–C_4 alkenes. The rates of oxidation for the alkanes are about the same as the corresponding alkenes at 300–350°C. By virtue of the lower activation energies for the two alkanes, their rates would be higher than that of the alkenes at lower temperature; this is different from that obtained over the other metal oxide catalysts, such as Co_3O_4, Cr_2O_3, etc. (*11*). The rate of CO oxidation is greater than the hydrocarbons.

The Kinetic Isotopic Effect

For the purpose of gaining some information about the rate-determining step and the adsorbed state of the hydrocarbons on the surface, the rate of oxidation of C_2D_4, C_2D_6 and CD_3CHCH_2 were also determined. For such studies, the rates for the hydrogen and the deuterated compounds were determined alternately to insure their comparability. The results are shown in Table 5.

The kinetic isotopic effect for C_2H_4 oxi-

TABLE 4

RATE OF CO_2 PRODUCED OVER NiO(I)[a]

Reactant	350°C	300°C
C_2H_4	0.017	0.0030
C_3H_6	0.036	0.0062
C_4H_8-1	0.052	0.0090
trans-C_4H_8-2	0.035	0.0061
i-C_4H_8	0.071	0.012
C_2H_6	0.018	0.0053
C_3H_8	0.038	0.0084
CO	0.137	0.0236

[a] ml STP/m^2-min (4% O_2, 1% HC, 0.1% H_2O).

TABLE 5
KINETIC ISOTOPIC EFFECT

	k_D/k_H	(°C)
C_2H_4 vs C_2D_4	1	(300)
CD_3CHCH_2 vs C_3H_6	0.75	(300)
C_2D_6 vs C_2H_6	0.45	(300)
C_2D_6 vs C_2H_6	0.60	(400)

dation is one and suggests that splitting of the C–H bond is not involved in the rate-determining step. The rate of adsorption of ethylene or reaction between oxygen and the double bond of ethylene adsorbed on the surface may be the rate-determining step with the C_2H_4 molecules adsorbed on the surface through the π bond. There is ample evidence in the literature on such π bond donor–acceptor type of adsorption for C_2H_4 on transition metal ions (*7*). On the other hand, the kinetic isotopic effect for C_2H_6 oxidation is 0.45–0.60. This indicates that the rate-determining step may be either the adsorption of ethane as C_2H_5 radical with breaking of the C–H bond if the slow step is the chemisorption of the ethane molecules, or the interaction between the adsorbed O_2 and either gas phase or physically adsorbed C_2H_6 through attack at the C–H bond. In the case of CD_3CHCH_2, the kinetic isotopic effect was found to be 0.75. Several previous reports on the partial oxidation of propylene over metal oxide catalysts have found that abstraction of the allyl hydrogen followed by weakening the π bond through adsorption to form a symmetrical π-allyl complex on the surface as the most probable adsorbed species (*12*). If the rate of formation of this species were the overall rate-determining step, one would expect an isotope effect.

The Competitive Oxidation

Moro-oka and Ozaki (*6*) have measured the relative adsorption strength for various hydrocarbons over several supported metal oxide catalysts using the competitive oxidation techniques. Hofer, Guessey, and Anderson (*13*) reported that CO enhanced the oxidation of C_2H_4 while C_2H_4 inhibited the oxidation of CO over several metal oxide catalysts. The results obtained on several pairs of hydrocarbons which include C_2H_4 as one component are shown in Table 6. In all cases, mutual retardation was observed and the degree of retardation was found to be slightly dependent on the partial pressures, that is, increasing partial pressure of A with respect to that of B could enhance the retardation effect of A on B. The retardation effect was found to be completely reversible.

The retardation effect among the hydrocarbons follows the trend that the larger the n values of Eq. (1) (weaker in adsorption strength) and Table 3 the more it is susceptible to be retarded, this is the same trend as that established by Moro-oka and Ozaki (*6*). Whether the retardation was due to competition for available oxygen on the surface or for adsorption sites between the hydrocarbons is difficult to differentiate based on the present results alone. The similarity in the kinetic parameters among the various hydrocarbons, the common cause for initial decrease of activity and the fact that the total amount of O_2 consumed for mixed hydrocarbons was less than that which would be consumed by the component with higher rates if existing alone at the same partial pressure favor the mechanism of hydrocarbons competing with each other and O_2 for the adsorption sites on the surface.

The Role of Some Oxygenated Compounds and Poisons

Although no stable reaction intermediate was detected from the mass spectra of the

TABLE 6
COMPETITIVE OXIDATION OVER NiO(I)[a]

Hydrocarbon				
A	B	p_A/p_B	$R_A/(R_A)^0$	$R_B/(R_B)^0$
C_2H_4	CO	0.2	0.28	0.75
C_2H_4	C_3H_6	~1	0.4	0.6
C_2H_4	i-C_4H_8	0.7	0.38	0.65
C_2H_4	C_3H_8	1.5	0.70	−0.67

[a] $(R_A)^0$, $(R_B)^0$, Rate of CO_2 formation from A and B separately at the same partial pressures at which they exist in the mixture.

gas phase over the catalyst, it is thought that a study of the oxidation of some of the possible reaction intermediates and their effect on the oxidation rate of C_2H_4 might furnish some information towards the understanding of the reaction. The following compounds were used:

1. **Acetic acid.** When acetic acid was introduced to the catalyst in the absence of O_2 or hydrocarbon at 100–300°C, an amount equivalent to a complete monolayer was found to be taken up with near zero equilibrium pressure. No detectable CO_2 was evolved and suggests no appreciable reaction with the lattice oxygen. In the presence of O_2 in the gas phase, CO_2 formation was detected in the vicinity of 150°C and increased with increasing temperature. At 300°C, the rate of oxidation of acetic acid at near monolayer coverage and zero partial pressure was about 20 times that of C_2H_4 at $p_{C_2H_4}$ of about 0.5%. The rate decreased with time or the surface coverage of acetic acid. When there was excess acetic acid in the gas phase, the rate was even faster than that at full coverage and zero partial pressure. Injection of acetic acid into the reaction stream containing $C_2H_4 + O_2$ was found to temporarily suppress the oxidation of C_2H_4, but the oxidation of C_2H_4 resumed its original rate upon completion of the acetic acid oxidation. The adsorption of acetic acid was found to precede its oxidation.

2. **Acetaldehyde.** The oxidation of CH_3CHO was found to be quite similar to that of acetic acid in both its rate and adsorption behavior. Again it temporarily and reversibly suppressed the hydrocarbon oxidation with no permanent effect.

3. **Ethylene oxide.** The oxidation of C_2H_4O to CO_2 was found to be 5–7 times as fast as that of C_2H_4 at the same partial pressures of ~1%. The oxidation rate was approximately first order with respect to both O_2 and C_2H_4O. Adsorption of ethylene oxide at partial pressure of 1% was about 10% of a monolayer, so it was not as extensive as that of CH_3COOH or CH_3CHO.

On the basis of the fast oxidation rates of CH_3CHO, CH_3COOH and CO obtained, none of these compounds could be excluded as the possible reaction intermediate for the oxidation of C_2H_4 to CO_2. If any one of them were the intermediate, the rate-determining step of the complete oxidation of C_2H_4 must be prior to the formation of such intermediates. In the case of ethylene oxide, at very low partial pressure of C_2H_4O, the rate of oxidation could be comparable to that of the C_2H_4. However, the absence of an induction period and the large differences in the partial reaction order with respect to oxygen argues against the possibility of oxidation of C_2H_4O, if it were an intermediate, to be rate-determining.

4. **SO_2 and HCl.** In addition to water, SO_2 and HCl which represented the usual types of catalyst poisons were injected into the reacting stream to test their effect on the C_2H_4 oxidation. The rate of C_2H_4 oxidation as a function of SO_2 added is shown in Fig. 6. All of the SO_2 injected was immediately taken up by the catalyst with no SO_2 left in the gas phase. The surface coverage given in the graph was calculated using a cross-sectional area of 26 Å^2/SO_2. The catalyst was poisoned not only for the hydrocarbon oxidation but also for CH_3COOH oxidation as well. As shown in Fig. 6, the poisoning effect was not complete even at a SO_2 coverage of 90% of a monolayer. Whether the large dose of SO_2 required for complete poisoning of the catalyst is due to progressive piston type

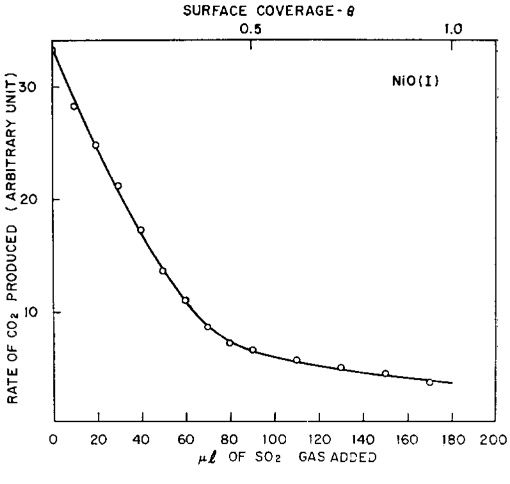

Fig. 6. Effect of SO_2 on oxidation of C_2H_4 over NiO(I).

nonselective adsorption of SO_2 on the cylindrically packed catalyst or represents actual adsorption in the order of surface heterogeneity with the catalytically active sites not preferentially adsorbed by SO_2 cannot be resolved from our data. Anhydrous HCl gas injected into the reaction stream showed a similar poisoning effect as that caused by SO_2. The adsorption and poisoning effect of SO_2 and HCl are completely irreversible. Once the surface was poisoned, neither repeated hydrocarbon oxidation nor heating in a few percent of oxygen up to 800°C for as long as 2 days could restore its original activity. Washing with concd. HNO_3 and H_2O could restore the activity.

5. Others. CH_3NH_2 was found to undergo a very complicated reaction over NiO catalyst to give N_2O, NH_3 and other unidentified compounds. It also could temporarily and reversibly suppress the oxidation of C_2H_4.

When H_2O_2 in the form of 30% solution in water was injected into the $C_2H_4 + O_2$ reaction stream, the effect was the same as that produced by H_2O alone, inhibition to give a small negative fractional order.

The Effect of the Catalyst Surface

Several NiO catalysts have been used for the C_2H_4 oxidation studies in addition to the NiO(I) reported above. The designation and preparation of the catalysts are as follows:

NiO(II) was NiO powder of reagent grade purchased from J. T. Baker Company. Emission spectroscopic analysis showed 0.2% Cr and 0.01% Fe with other impurities at the level of 0.001% or less.

NiO(III) was NiO powder, Specpure grade, of Johnson Mattey Co. Ltd. It was the starting material for NiO(I) as described in the previous section.

NiO(IV) was NiO crystals prepared from NiO(III) using the same procedures as that used for NiO(I) except Pt crucible and 1100°C were used instead of gold crucible at 960°C. Emission spectroscopic and X-ray fluorescence analyses showed no Pt present. The crystals are all octahedrons exposing the (III) face the same as that for NiO(I).

NiO(IV-W) was NiO(IV) crystal washed with hot aqua regia followed repeatedly with dil HNO_3 and distilled water.

NiO(IV-C) was obtained by crushing NiO(IV-W) in an agate mortar and pestle, followed by washing with HF, HNO_3 and repeatedly with dil HNO_3 and distilled water.

The surface areas of these catalysts are listed in Table 1. Prior to the oxidation runs, the samples were usually heated in a flow of N_2 with a few percent of O_2 to 800°C for several hours except NiO(IV-C) for which the first heating was only 550°C and subsequent heatings at 800°C. Since this phase of the work was done during the exploratory stage prior to the realization of how important the water inhibition effect can be, all the rate measurements were made with dry inlet gas at constant flow rate. In the log–log plots, the rate of CO_2 formed was again found to obey the empirical power law:

$$R = k' p_{O_2}{}^{m'} p_{HC}{}^{n'}$$

The m' and n' values thus obtained are expected to be smaller than their corresponding m and n values obtained at constant partial pressure of H_2O. The results are listed in Table 7. It is shown that the m' and n' values are temperature independent with the exception of NiO(IV) for which n' decreases and m' increases with decreasing temperature. At temperatures below 300°C, the reaction over NiO(IV) was negative fractional order with respect to $p_{C_2H_4}$. Such negative coefficients for hydrocarbon oxidation have also been found for C_2H_4 oxidation over Pt and Pd catalysts (*11, 14*). Therefore, it is suspected that a small amount of Pt from the crucible could have been incorporated into the catalyst although analytical results gave no indication of Pt present. The fact that this anomaly was removed in the results over NiO(IV-W) and NiO(IV-C) supports the contention of Pt contamination. These results are included in this report to illustrate the high sensitivity of catalyst activity towards certain catalytically active im-

TABLE 7
KINETIC PARAMETERS FOR OXIDATION OF C_2H_4 OVER NiO[a]

Catalyst	Temp (°C)	m'	n'
NiO(I)	245	0.41	0.23
	289	0.30	0.25
	345	0.37	0.16
	382	0.37	0.22
NiO(II)	260	0.42	0.43
	335	0.34	0.42
	388	0.37	0.42
NiO(III)	237	0.25	0.33
	328	0.29	0.40
NiO(IV)	263	0.63	−0.37
	317	0.59	0.07
	343	0.60	0.15
	390	0.43	0.23
NiO(IV-C)	250	0.35	0.33
	268	0.42	0.38
	327	0.38	0.39
	374	0.42	0.38
NiO(IV-W)	284	0.41	0.28
	317	0.42	0.25
	345	0.36	0.34
	375	0.38	0.33

[a] $\Delta CO_2/\Delta t = k'(p_{O_2})^{m'}(p_{C_2H_4})^{n'}$, $p_{H_2O} \simeq p_{CO_2}$.

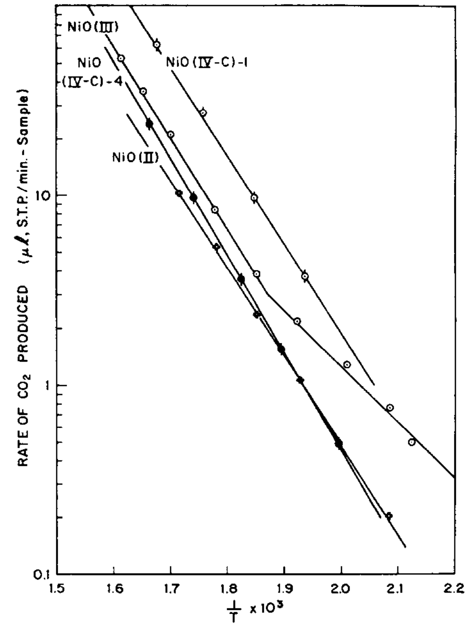

FIG. 7. Arrhenius plots for C_2H_4 oxidation: (✙) NiO(II), 1.6 m²; O_2, 4.5%; C_2H_4, 2.0%; (⊙) NiO(III), 2.1 m²; O_2, 10.5%; C_2H_4, 0.8%; (⦶) NiO(IV-C)-1, 0.75 m²; O_2, 6.6%; C_2H_4, 3.9%; (●) NiO(IV-C)-4, 1.2 m²; O_2, 11.8%; C_2H_4, 3.3%.

purities. This is not surprising, as the specific activity for C_2H_4 oxidation over Pt is about 1 × 10⁴ times that for NiO under the same ambient conditions (*11*). On the other hand, NiO(II) and NiO(III) did not show much difference even though they were obtained from different sources and with more significant differences in the impurities present. The variations in the m' and n' values of the various NiO catalysts except NiO(IV) are relatively insignificant.

The Arrhenius plots for C_2H_4 oxidation over the various NiO catalysts are shown in Fig. 7. They are only slightly lower than that over NiO(I). This difference may be attributed to the fact that the p_{H_2O} effect was not corrected for the results in Fig. 7. The reason why there is a change of slope for NiO(III) but not for the others is not known.

The rate of C_2H_4 oxidation at 300 and 350°C under the conditions of 4% O_2, 1% hydrocarbon and 0–0.05% H_2O are listed in Table 8. The freshly ground NiO crystal after 550°C sintering once, NiO(IV-C)-1, gave the highest specific activity. This sample after repeated sintering at 800°C decreased its specific activity to a value approximately equal to those of the powders [see NiO(IV-C)-5 vs NiO(II)]. The differences in the rate of C_2H_4 oxidation among the various catalysts are small; this is different from that observed over Cr_2O_3 catalysts (*15*). However, it is of

TABLE 8
RATE OF CO_2 PRODUCED FROM C_2H_4 OXIDATION[a]

Catalyst	350°C	300°C
NiO(I)	0.017	0.0030
NiO(II)	0.023	0.0041
NiO(III)	0.020	0.0040
NiO(IV)	0.016	0.0027
NiO(IV-W)	0.016	0.0030
NiO(IV-C)-1	0.053	0.012
NiO(IV-C)-5	0.023	0.0030

[a] ml STP/m²-min (4% O_2, 1% C_2H_4).

interest to note that the rates over the (111) face of NiO(I) and NiO(IV-W) are the same while those over the crushed-resintered crystals and powders with random distribution of crystalline faces exposed are all slightly higher. Whether this is due to genuine geometric effect or fortuitousness requires more detailed study.

The Adsorption Studies

Efforts to measure the adsorption of O_2 and hydrocarbon *in situ* using the mass spectrometric method failed to detect any adsorption even though the sensitivity of the instrument was amply sufficient to detect 0.001 ml/min of gas uptake. This may be due to the inability of removing all oxygen and hydrocarbon adsorbed on the surface prior to the adsorption run by sweeping with N_2 or He at 800°C. Therefore, the indirect method of measuring adsorption using a conventional volumetric apparatus together with a CEC 103 mass spectrometer with batch inlet system was used. Prior to each series of runs (designated by Roman numerals), the surface was outgassed at 450–500°C for several hours to 1×10^{-6} mm Hg. Typical adsorption results at 200–300° are shown in Fig. 8 and Table 9. The sequences of the runs in each series are designated by the Arabic numerals and the sample was outgassed at the adsorption temperature to 1×10^{-6} mm Hg before proceeding to the next run. The amount adsorbed for both O_2 and hydrocarbon are no greater than a few percent of a monolayer in agreement with those reported in the literature (*9, 16*). Hydrocarbons adsorbed could only be removed from the surface by heating in a few Torr of O_2 at a temperature higher than the reaction temperature. The initial fast adsorption of oxygen could only be regenerated by outgassing at 450°C and above. The slow adsorption of O_2 decreased with increasing number of O_2 adsorption runs

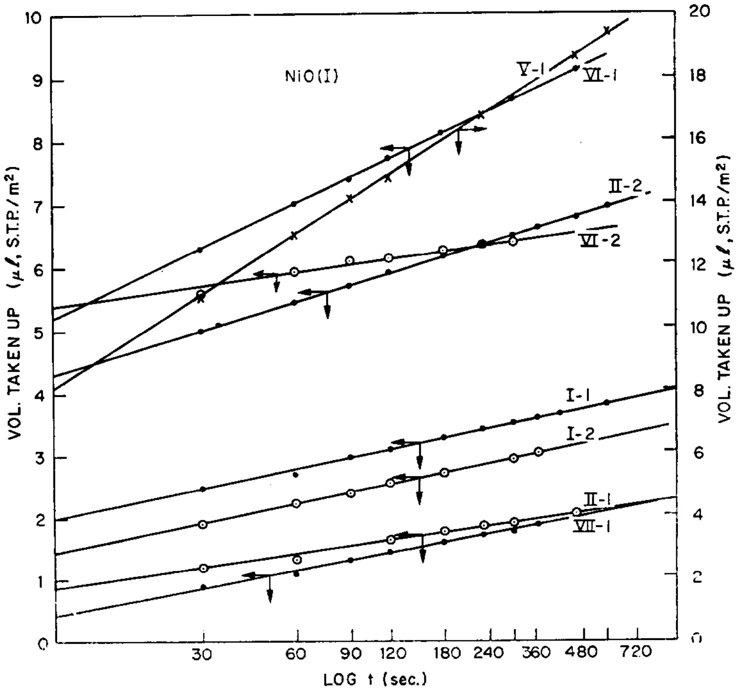

FIG. 8. Adsorption of O_2 and C_3H_6 on NiO(I) (see also Table 9 and text for pretreatment conditions): (I-1) O_2, 200°C; (I-2) C_3H_6, 200°C;(II-1) C_3H_6, 200°C, (II-2) O_2, 200°C; (V-1) O_2 + C_3H_6 (1.3:1), 200°C) V(I-1) O_2, 300°C; (VI-2) C_3H_6, 200°C; (VII) O_2, 150°C.

TABLE 9
UPTAKE OF O_2 AND C_3H_6 IN THE FIRST MINUTE ON NiO(I)[a]

Series-run no.	Gas	Vol uptake mml STP/m²	Surface coverage (molec/10 000 Å²)
I-1	O_2	2.8	7.4
I-2	C_3H_6	2.2	5.8
I-3	O_2	1.8	4.7
II-1	C_3H_6	1.4	3.7
II-2	O_2	5.45	14.4
II-3	C_3H_6	0.6	1.6
III-1	H_2O	(~10)	26
III-2	O_2	0.5	1.3
IV-1	H_2O	(~10)	26
IV-2	C_3H_6	0.4	0.1
V-1	$O_2 + C_3H_6$ (1.3:1)	10.9	29

[a] $T = 200°C$; $p_{O_2} \sim p_{C_3H_6} \sim 1.1$–$1.5$ Torr. Prior to each series of runs, the sample was outgassed at 450°C. Between successive runs in each series, the sample was outgassed at 200°C.

and prolonged heating in vacuum at 500°C was required to restore its original rate. The rates of adsorption were found to obey the Elovich type equation (Fig. 8) and thus imply the existence of a wide distribution of adsorption site energies over the surface. In view of the fact that CO_2 was evolved immediately upon admitting the reactants in the flow reaction system, the slow adsorption process probably does not contribute significantly to the oxidation reaction. This limits the catalytically active sites to only those responsible for the initial fast adsorption, but not necessarily all of those sites. It would appear that the fraction of surface sites that are catalytically active at any one time could be no more than 1%. These are not necessarily fixed geometric sites.

Enhanced adsorption of O_2 on C_3H_6 or C_3H_8 presorbed surface or the reversed case for C_3H_6 on surface presorbed with O_2 was observed. The adsorption of C_3H_6 on surface presorbed with O_2 at 300°C is greater than that with O_2 at 200°C. Part of the presorbed O_2 was removed by the hydrocarbon and vice versa. However, mass spectrometric analysis of the gaseous phase showed no CO_2 or other product present. Thus, the reaction products in such cases are probably adsorbed on the surface and can only be removed by high temperature outgassing.

Upon admitting a mixture of O_2 and hydrocarbon to the catalyst, the total pressure of the static system decreased at a rate much greater than the sum of the amount taken up if the two components were admitted separately with outgassing in between. Mass spectrometric analy-

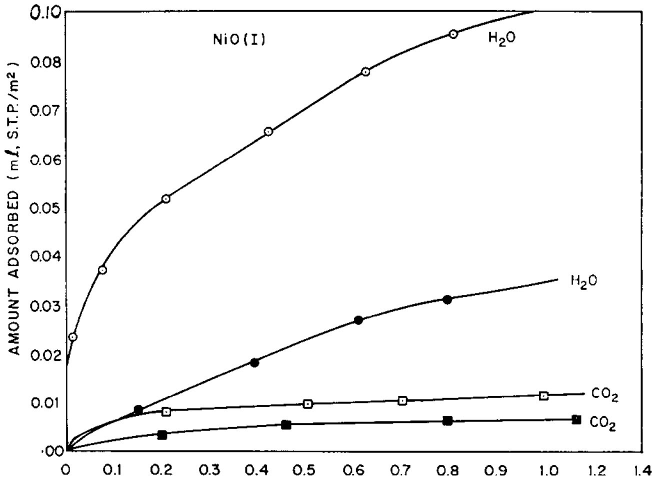

FIG. 9. Adsorption of H_2O and CO_2 over NiO(I) at 200°C: (⊙ ⊡) on 450°C outgassed surface; (● ■) rerun after ⊙ and ⊡, respectively, outgassed at 200°C.

sis showed significant amount of CO_2 formation.

The adsorption isotherms for CO_2 and H_2O at 200°C on the surface outgassed at 450°C are shown in Fig. 9. For both cases, the adsorption was not completely reversible at the adsorption temperatures. When $p_{CO_2} \lesssim p_{H_2O}$, the prevailing condition of the reactions, the amount of CO_2 adsorbed was much smaller than that of H_2O. This is in agreement with the fact that H_2O inhibits the oxidation reaction while CO_2 does not. The surface coverage of H_2O was much larger than that of O_2 and hydrocarbon, yet the catalytic reaction was not completely stopped. Therefore, the water adsorbed on the surface was not adsorbed selectively at the fixed geometric active sites if such were the case. The inhibition effect is probably through general steric blocking and the adsorption of water is an ion dipole type interaction.

When the surface was pretreated with water and evacuated so that only the irreversibly adsorbed H_2O was left on the surface, the adsorption of O_2 and hydrocarbon was greatly reduced. Since water is produced in the oxidation of the hydrocarbons, this would mean that the surface available for catalyzing the oxidation reaction would be reduced to even less than the 1% available for adsorption under water-free condition. In retrospect, it is not surprising that the adsorption of hydrocarbon and O_2 could not be determined *in situ* where the flow system could hardly meet the stringent conditions required to obtain an adsorbate-free surface.

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