

The Oxidation of Hydrocarbons and CO over Metal Oxides

III. Co_3O_4

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The catalytic oxidation of CO, C_2H_4 , and C_2H_6 has been studied over Co_3O_4 and Co_2O_3 supported on alumina. At low temperatures the reaction kinetics can be described by the general expression of

$$\text{Rate} = k p_{\text{O}_2}^m p_{\text{CO}}^n (\text{or HC}) p_{\text{H}_2\text{O}}^{-l} e^{-\Delta E/RT},$$

where l , m , and n are in the range of 0.3 to 0.5 and ΔE 20-23 kcal/mol. At high temperatures the rates are controlled by bulk diffusion. The specific catalytic activity over the Co_3O_4 powder is the highest among the various metal oxides previously studied.

Mutual retardation was observed between CO and C_2H_4 when they coexist in the gas phase. NO can reversibly inhibit the oxidation of CO at 200°C without reaction. A few ppm of SO_2 in the gas phase can cause irreversible reduction of the Co_3O_4 catalytic activity at 500°C or below. At 550°C or above, finite equilibrium between the SO_2 concentration in the gas phase and the reduction in activity can be reached, and the SO_2 inhibition becomes reversible.

The activity of the supported Co_3O_4 catalysts varies over several orders of magnitude depending on the method of preparation. In general, the mechanical mixtures of Co_3O_4 and colloidal alumina are much more active than those prepared by impregnation. The nature of the diluents used in the mixtures also influences the activity. Heating the supported catalysts to 850°C deactivates the catalysts severely due to (1) sintering of the Co_3O_4 , (2) sintering of the diluents to form mass transfer barrier, and (3) reaction to form the catalytically inactive CoAl_2O_4 .

INTRODUCTION

In the application of heterogeneous catalytic oxidation to the removal of CO and hydrocarbons from the automotive exhaust, it is of importance to know the kinetic parameters of such oxidation reactions. However, in the literature, relatively few studies have been reported on the kinetics of the complete oxidation of CO and hydrocarbons to CO_2 and H_2O , the desirable reaction for the automotive emission control. It has been the purpose of this investigation to determine the kinetic parameters, such as specific reaction rates per unit surface area, their dependency on the ambient conditions and the mutual effect of reactants co-

existing in the gaseous phase, and any reaction poisons present over various noble metal and base metal oxide catalysts. The results on Pt, Pd, Au, NiO, and Cr_2O_3 have been reported previously (1-3). In this paper, the results over Co_3O_4 will be reported.

It has been reported (4, 5) and also found in this study that among all the base metal oxides studied, Co_3O_4 gives the highest specific activity for the complete oxidation of CO and hydrocarbons. Anderson and his co-workers (4) found that the activity of Co_3O_4 supported on γ -alumina was several orders of magnitude less than that of the unsupported oxide. Pattison and several

other workers *et al.* (6, 7) reported the formation of cobalt aluminate upon heating a mixture of Co(NO₃)₂ and hydrated or γ -aluminas at 870°C and above. Therefore, it is of interest to examine the effect of the support and the method of supported catalyst preparation on the catalytic activity for the Co₃O₄-Al₂O₃ system.

EXPERIMENTAL METHODS

Preparation of the Co₃O₄ Catalysts

Three Co₃O₄ preparations were used. Co₃O₄ (I) was Specpure grade Co₃O₄ purchased from Johnson-Matthey Co. Ltd. The surface area of this oxide was found to remain at 0.44 m²/g after heating at 850°C for 2 days. Therefore, the material was probably prepared at high temperature and there was no lower temperature version of this preparation. Co₃O₄ (II) was prepared by calcining Co₂O₃ at 400°C for 16 hr. The latter was prepared using the method as described by Merrill *et al.* (8). The Co₃O₄ was further heated at 600° and 850°C to give Co₃O₄ (II-600) and Co₃O₄ (II-850), respectively.

Co₃O₄ (III) was prepared by slowly mixing Co(NO₃)₂ aqueous solution with NH₄OH to form a precipitate which dried at 150°C followed by heating in air at 400°C for 1 day. The Co₃O₄ was further heated in air at 600° and 850°C to give Co₃O₄ (III-600) and Co₃O₄ (III-850).

Since Co₂O₃ is reported to be unstable and to convert to Co₃O₄ at above 350°C, all Co₃O₄ catalysts were heated at 400°C or above. At the vicinity of 900–950°C, Co₃O₄ could lose oxygen to form CoO, therefore, no heat treatment was performed at above 850°C. To avoid any possible contamination of the catalyst by catalytically active impurity such as Pt, all the heating was done in either porcelain or gold crucibles. The oxides after the appropriate heat treatments were washed with dilute HNO₃ followed by distilled water and reheated briefly at 500°C prior to being used for the oxidation studies. The surface areas of the catalysts were measured by Kr adsorption at -195°C and calculated using BET equation, the results are listed in Table 1.

TABLE 1
SURFACE AREA OF Co₃O₄

Catalyst	Highest pretreatment temp (°C)	Surface area (m ² /g)
Co ₃ O ₄ (I)	>850	0.44
Co ₃ O ₄ (II)	400	38.8
	600	10
	850	0.93
Co ₃ O ₄ (III)	400	24.1
	600	5.0
	850	1.2
CoAl ₂ O ₄	850	11.3

The CoAl₂O₄ was purchased from City Chemical Co.

Preparation of the Supported Co₃O₄ Catalysts

Two types of catalysts were prepared. The first type was made by a simple impregnation of the support. The second type was a mechanical mixture of the support and Co₃O₄.

1. Co₃O₄-Al₂O₃ (Im) Series

These samples were prepared by the impregnation of the support with either Co(NO₃)₂ or Co(CH₃COO)₂ aqueous solutions. The support materials and their surface areas are listed in Table 2. After impregnation, the Co-coated aluminas were dried at 150–200°C followed by calcination in air at 600° or 850°C for 1 day. In the case of Co₃O₄-Al₂O₃ (ImNN)* and Co₃O₄-Al₂O₃ (F) (ImNN) the wet material after impregnation was exposed to a stream of NH₃ to convert the Co(NO₃)₂ into a hydrated oxide. It was then dried slowly at less than 150°C, followed by 200, 600 and/or 850°C heating in air.

2. Co₃O₄-DAL Series

These samples were prepared by blending thoroughly the Co₃O₄ (II) or Co₃O₄ (III)

*See Table 2 for catalysts composition.

TABLE 2
 SUPPORTED Co_3O_4 CATALYSTS

Catalyst	Method of preparation ^a	Support	Support surface area ^b (m ² /g)	Source of Co ^c	Wt% of Co_3O_4
Co_3O_4 -DAL (1-9)	M	Dispall ($\gamma\text{-Al}_2\text{O}_3$)	133 (600°C) 91 (850°C)	Co_3O_4 II—400°C	1-45
Co_3O_4 -DAL (10-12)	M	Dispall ($\gamma\text{-Al}_2\text{O}_3$)	91 (850°C)	Co_3O_4 III—400°C	8-10
Co_3O_4 -DAL (13)	M	Dispall ($\gamma\text{-Al}_2\text{O}_3$)	91 (850°C)	Co_3O_4 III—850°C	10.1
Co_3O_4 -Linde A	M	Linde A ($\alpha\text{-Al}_2\text{O}_3$)	Av 0.34 μm diam	Co_3O_4 II—400°C	9.2
Co_3O_4 -Linde B	M	Linde B ($\gamma\text{-Al}_2\text{O}_3$)	Av 0.05 μm diam	Co_3O_4 II—400°C	15.4
Co_3O_4 -Cab-O-Sil	M	Cab-O-Sil (SiO_2)		Co_3O_4 II—400°C	13.3
Co_3O_4 -Mullite	M	Mullite		Co_3O_4 II—400°C	9.1
Co_3O_4 - Al_2O_3 (K) (ImN)	Im	Kaiser $\gamma\text{-Al}_2\text{O}_3$	190	$\text{Co}(\text{NO}_3)_2$	10.4
Co_3O_4 - Al_2O_3 (ImN1)	Im	Dispall—600°C	133	$\text{Co}(\text{NO}_3)_2$	17.2
Co_3O_4 - Al_2O_3 (ImN2)	Im	Dispall—850°C	91	$\text{Co}(\text{NO}_3)_2$	17.3
Co_3O_4 - Al_2O_3 (ImA)	Im	Dispall—600°C	133	$\text{Co}(\text{AC})_2$	5.5
Co_3O_4 - Al_2O_3 (ImNN)	Im	Dispall—600°C	133	$\text{Co}(\text{NO}_3)_2 + \text{NH}_3$	3.3
Co_3O_4 - Al_2O_3 (F) (ImNN)	Im	Fiberball ^d	53	$\text{Co}(\text{NO}_3)_2 + \text{NH}_3$	6.1

^a M, mixing; Im, impregnation. In each case calcination at 600°C and/or 850°C following drying at 200°C.

^b The surface areas are the surface area of the support alone after heated at 600° or 850°C.

^c Surface areas of the source Co_3O_4 ; see Table 1.

^d Fibrous support manufactured by UGINE-KUHLMANN INDUSTRIES.

(both from 400°C calcined) with a 20% aqueous solution of Dispall (a high purity colloidal alumina from Continental Oil Co.). The blended gel material was dried at 150–200°C followed by calcination at 600 and/or 850°C for at least 1 day. The composition, starting material, and the surface area of these samples are listed in Tables 2 and

 TABLE 3
 SURFACE AREA OF Co_3O_4 -DAL CATALYSTS

Catalyst	Wt% Co_3O_4	Pretreatment temp (°C)	Total surface area (m ² /g catalyst)	Estimated ^a Al_2O_3 surface area (m ² /g Al_2O_3)
Co_3O_4 II—400°C	100	400	38.8	0
Co_3O_4 II—600°C	100	600	10	0
Co_3O_4 II—850°C	100	850	0.93	0
Dispall—200°C	0	200	~250	~250
Dispall—600°C	0	600	133	133
Dispall—850°C	0	850	91	91
Co_3O_4 -DAL(1)	25.2	600	143	183
Co_3O_4 -DAL(1)	25.2	850	102	128
Co_3O_4 -DAL(2)	3.5	600	201	207
Co_3O_4 -DAL(2)	3.5	850	139	142
Co_3O_4 -DAL(3)	45	600	89	142
Co_3O_4 -DAL(3)	45	850	43	89

^a Assuming Co_3O_4 area in 600°C mixed catalyst = 24.4 m²/g Co_3O_4 and 850°C catalyst, 5.5 m²/g Co_3O_4 (the mean value of Co_3O_4 II 400–600°C and 600–850°C).

3. An electron micrograph of the 600°C heated catalyst is shown in Plate 1.

3. *Co₃O₄-X Series*

These samples were prepared by the blending method similar to that described

above. Various supports were used. For Cab-O-Sil a high area SiO₂, the gel was prepared by the addition of NH₄OH to the aqueous suspension of Co₃O₄ and Cab-O-Sil. For the other supports, 5% oleic acid was used as the dispersing agent in order to mix

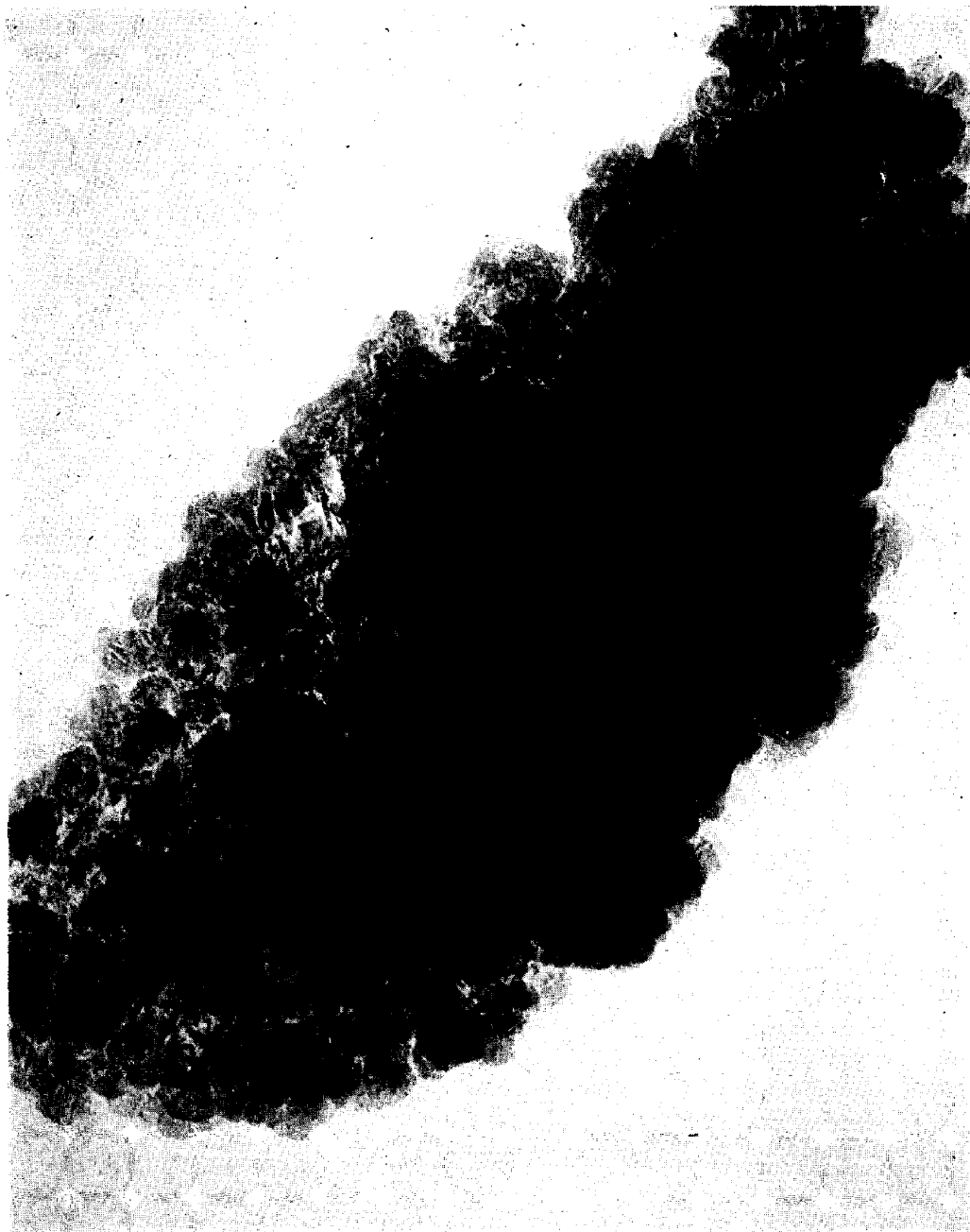


PLATE 1. Co₃O₄-DAL (10)—600°C.

the support and the Co_3O_4 . The same drying and calcining procedures were used as the others.

As a rule the 600°C calcined samples with Al_2O_3 , were grey in color while those after 850°C heating were blue. This suggests that formation of CoAl_2O_4 has taken place during the 850°C heating. No acid washing was applied to the supported catalysts to avoid dissolution of the supports.

The gases used were CP grade O_2 , CO , C_2H_4 , C_2H_6 , and NO . Helium was used as carrier gas. SO_2 was supplied as 0.1% SO_2 in argon.

The composition of the inlet gas and that after passing over the catalyst were analyzed continuously using an on-line continuous inlet mass spectrometer (CEC 614). The procedures have been previously described (1). Prior to each run, the sample was heated to 500°C and cooled down to the reaction temperature in He containing 1–2% oxygen. A liquid nitrogen cooled trap was put around the gas inlet line for runs designated as 0% H_2O .

RESULTS AND DISCUSSION

General Characteristics of the Reactions

It is found that CO , C_2H_4 , and C_2H_6 were stoichiometrically converted to CO_2 and H_2O over the Co_3O_4 catalysts both supported and unsupported. Over the Co_3O_4 powders, the catalytic activity improved considerably after washing with dilute HNO_3 and H_2O . But the initial activity of the washed catalysts suffered a self-deactivation period which could reduce the activity by as much as 70%. After the initial deactivation, the activity became relatively stable and was still higher than that of the unwashed samples. Although no deterioration in activity was observed once the initial deactivation was over, it was found that the activity and the reproducibility was better if the sample was preheated at 400°C or above in a stream of He containing 1–2% of oxygen dried by a liquid-nitrogen trap. This was probably due to the fact that H_2O inhibits the reaction and the heat treatment was needed to reproduce a water-free surface. For reaction at 125°C or below, there

was a gradual decrease of activity with time probably attributable to the adsorption of CO_2 and/or H_2O or other reaction intermediates on the surface. Any water inadvertently entering the system could also severely inhibit the reaction at the low temperatures. Therefore, the results at temperatures below 150°C were generally less reproducible and are not reported in this paper. The large surface area of the supports could serve as a sink and reservoir of H_2O and interfere with the activity determination, therefore CO oxidation over the supported catalysts were generally conducted at 0% H_2O . In the case of hydrocarbon oxidation, the presence of H_2O was unavoidable but the reactions were generally conducted at 300°C and above where the H_2O inhibition effect is relatively less severe.

To avoid the possibility of reducing the surface by CO or C_2H_4 , oxygen richer than the stoichiometric ratio was the prevailing condition for the oxidation experiments. However, exposure of the catalyst to oxygen deficient ambient or even in He containing 1–2% CO with no O_2 for a period up to 20 min at 200°C showed no adverse effect on the catalytic activity. Long time exposure to the reducing condition or at higher temperature was not attempted.

For the determination of the kinetic parameters, one would like to have the reactor maintained at isothermal conditions and the percentage of the conversion to be as low as possible. These conditions were easier to attain for the less active catalysts such as NiO and Cr_2O_3 . In the case of Co_3O_4 , its high activity for CO oxidation (and somewhat less activity for C_2H_4 oxidation) makes it difficult to maintain the desirable conditions. In this study, the reaction at each set of temperature-ambient composition conditions was allowed to reach a constant rate. Under such quasi steady state conditions, the heat of reaction was used to maintain the constant temperature of the reactor with proportionally less heat supplied from the furnace. The catalyst temperature was measured by a thermocouple attached to the reactor wall. Although undoubtedly the temperature of the catalyst

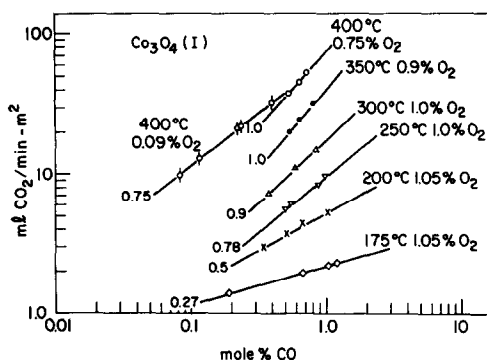


FIG. 1. Rates of oxidation of CO over Co₃O₄ (I), 0% H₂O, constant p_{O_2} .

itself is somewhat higher than that at the reactor wall measured by the thermocouple, the difference is small because of the use of helium as a carrier gas. Within limited range of reaction conditions, the error due to this temperature difference is probably small as evidenced by the following observations: (1) the absence of the so called "ignition" phenomenon observed over many of the highly exothermic reactions, and (2) the linearity obtained over a relatively wide range in the log-log plots for reactions rates versus the partial pressures of one of the reactants with the other reactant partial pressures nearly constant (Figs. 1-4). Furthermore, as it will be shown later, at high temperature where the percent of conversion is high, the activation energy of the reaction becomes small (a few kcal/mole) due to mass transfer problems. In that case, the

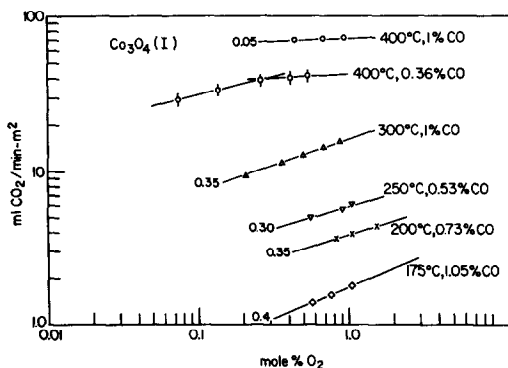


FIG. 2. Rates of oxidation of CO over Co₃O₄ (I), 0% H₂O, constant p_{CO} .

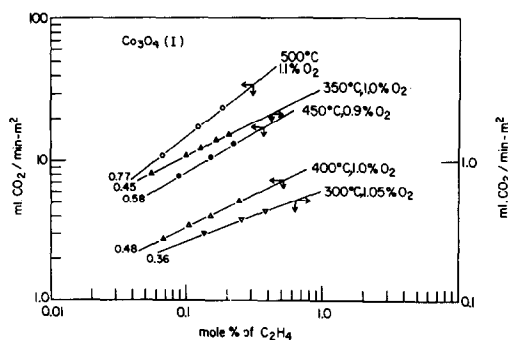


FIG. 3. Rates of oxidation of C₂H₄ over Co₃O₄ (I), constant p_{O_2} , 0.2-0.5% H₂O.

effect of the nonisothermic condition on the reaction rate would be relatively small.

To approach the conditions of a differential reactor, i.e., to keep the percent of conversion low, is rather difficult for the very active catalysts such as Co₃O₄. In this study, only the results obtained at less than 30% conversion were used for the kinetic parameter evaluations and the average value of the inlet and outlet partial pressures of each reactants is taken as the partial pressure of that component over the catalyst. Because of these limitations, the kinetics of the reactions could only be studied within a relatively narrow range of temperatures, about the 200°C range.

Kinetic Parameters of the Reactions over Co₃O₄

The dependency of the reaction rates as a function of partial pressure of each of the reactants at constant temperature was de-

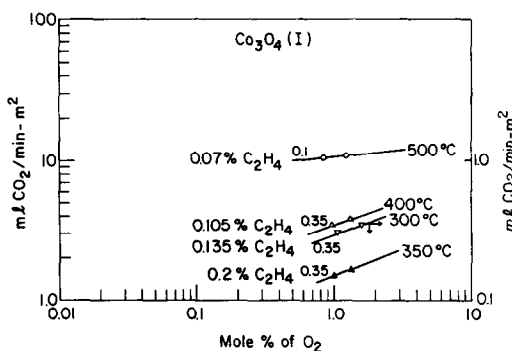


FIG. 4. Rates of oxidation of C₂H₄ over Co₃O₄ (I), constant $p_{C_2H_4}$, 0.2-0.5% H₂O.

TABLE 4
 KINETIC PARAMETERS OVER Co_3O_4^a

Reactant	Temp range (°C)	$-l(\text{NS})^b$	$m(\text{NS})^b$	$n(\text{NS})^b$	$f(\text{NS})^b$	$\Delta E(\text{NS})$ (kcal/mole)
CO	150-200	0.3 ± 0.1 (5)	0.46 ± 0.12 (10)	0.45 ± 0.10 (10)	0	20 ± 2 (6)
CO	300-350	0.1 ± 0.1 (4)	0.10 ± 0.04 (10)	0.93 ± 0.10 (10)	0.3 ± 0.1 (3)	5 ± 2 (5)
C_2H_4	275-450	0.35 ± 0.1 (5)	0.29 ± 0.07 (14)	0.51 ± 0.10 (14)	0	23 ± 2 (5)
C_2H_4	300-450	0.3 ± 0.1 (3)	0.33 ± 0.07 (8)	0.62 ± 0.08 (8)	0	21 ± 2 (3)

^a Rate = $k(p_{\text{O}_2})^m(p_{\text{CO or HC}})^n(p_{\text{H}_2\text{O}})^l(\text{flow rate})^f e^{-\Delta E/RT}$.

^b NS = number of samples used for averaging.

terminated by maintaining the partial pressure of one of the components fairly constant ($\pm 5-10\%$) and varying the partial pressure of the second reactant. Typical results are shown in Figs. 1-4. The rates are expressed in milliliters of CO_2 formed per minute per square meter of the Co_3O_4 surface which was determined by Kr adsorption and was found to remain constant after many oxidation runs. The linearity in the log-log plots suggests that the reactions can be kinetically expressed by the general power law, the same as that found over the other base metal oxides (1, 2).

$$R = k p_{\text{O}_2}^m p_{\text{CO}^n(\text{or HC})} p_{\text{H}_2\text{O}}^{-l} e^{-\Delta E/RT},$$

where R is the specific rates ml $\text{CO}_2/\text{min}\cdot\text{m}^2$, k is the rate constant, p_{O_2} , p_{CO} , p_{HC} , and

$p_{\text{H}_2\text{O}}$ are the partial pressures in mole % for O_2 , CO , hydrocarbon, and H_2O , respectively. The partial reaction orders are obtained from the slopes of the log-log plots. The apparent activation energies ΔE were obtained from the Arrhenius plots using rates obtained at different temperatures under one set of partial pressures (Figs. 5 and 6). The average kinetic parameters thus obtained and the number of points used for the averaging are listed in Table 4. In view of the fact that the reactions were not carried out under strictly isothermal and differential reactor conditions, a variation in the l , m , and n values of $\pm 10\%$ is not unexpected. The results show that the kinetic parameters are the same for the three different preparations of the Co_3O_4 powders

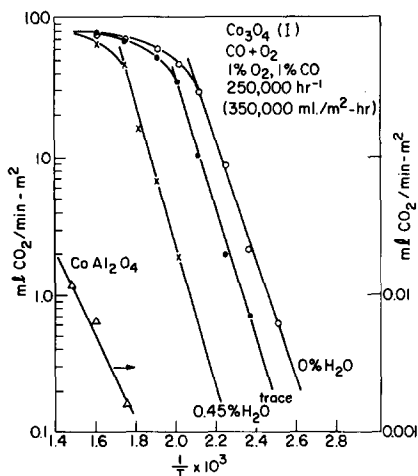


FIG. 5. Arrhenius plots for CO oxidation over Co_3O_4 (I) and CoAl_2O_4 .

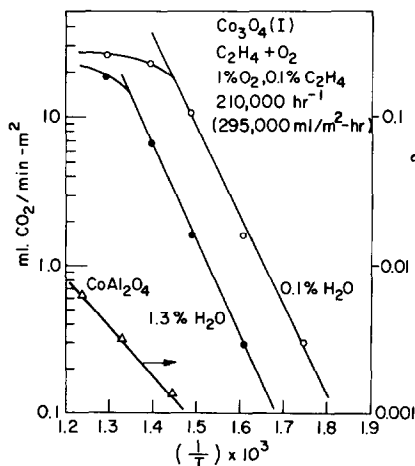


FIG. 6. Arrhenius plots for C_2H_4 oxidation over Co_3O_4 (I) and CoAl_2O_4 .

and that the pretreatment temperature makes little difference. It is shown that for both CO and C₂H₄, the slopes of the Arrhenius plots decrease with increasing temperature. Concomitantly, the m values decrease to zero while n values increase to near 1 with increasing temperature when the ambient composition is oxygen rich, in the case of CO/O₂ > 2, then $m \gg 0$ and $n \ll 1$. The bend in the Arrhenius plots shifts to higher temperature but of approximately the same specific reaction rates when the rates are suppressed by the presence of H₂O or other inhibitors. Furthermore, the reaction rates are independent of the flow rate of the gas at low temperature (high ΔE region) and become flow rate dependent to as much as half order at high temperatures when the Arrhenius plots are flat. All these observations suggests that the rate at high temperatures is controlled by bulk diffusion, the diffusion of the reacting molecules to the

external surface of the catalyst. The transition region between the low temperature intrinsic reaction rate-controlling region and that of bulk diffusion controlling at high temperature is generally considered to be controlled by the relative rates of the intrinsic reaction rate and the diffusion in and out of the pores. The sintered powdered catalysts undoubtedly have some pores but any quantitative treatment of the results in this region is not possible.

The lower rates for hydrocarbon oxidation delayed the onset of the diffusion control to higher temperatures and confirm the contention that the change in kinetic parameters with temperature originates from the inability of transferring the reacting molecules to the catalyst surface to meet the demand of the high intrinsic reaction rate.

The results at the lower temperature range where the intrinsic reaction rate is

TABLE 5
SPECIFIC RATES OVER Co₃O₄^a

Catalyst	CO + O ₂		C ₂ H ₄ + O ₂		C ₂ H ₆ + O ₂	
	T (°C)	R (ml CO ₂ / min-m ²)	T (°C)	R (ml CO ₂ / min-m ²)	T (°C)	R (ml CO ₂ / min-m ²)
Co ₃ O ₄ I	150	2.2	300	0.3	400	0.6
	200	28	350	1.8		
	300	70	400	10.5		
Co ₃ O ₄ II—600°C (diluted with Linde A)	150	1.0	300	0.3	400	1.3
	200	17	350	1.3		
	300	120	400	4.3		
Co ₃ O ₄ II—850°C	150	1.1	300	0.4	400	0.8
	200	20	350	1.5		
	300	60	400	5.0		
Co ₃ O ₄ III—600°C	150	2.3	300	0.45		
	200	28	350	2.2		
	300	95	400	9.5		
Co ₃ O ₄ III—850°C	150	1.2	300	0.3		
	200	21	350	1.1		
	300	35	400	3.5		
CoAl ₂ O ₄	300	0.003	400	0.0005		

^a CO + O₂, 1% O₂, 1% CO, 0% H₂O; C₂H₄ + O₂, 1% O₂, 0.1% C₂H₄, 0.1% H₂O; C₂H₆ + O₂, 1% O₂, 0.1% C₂H₆, 0.1% H₂O.

TABLE 6
OXIDATION OF CO + C₂H₄ OVER Co₃O₄ III—850°C

<i>T</i> (°C)	CO (%)	C ₂ H ₄ (%)	<i>R</i> _{CO} / <i>(R</i> _{CO}) ^o	<i>R</i> _{HC} / <i>(R</i> _{HC}) ^o
250°C	0.26	0.13	0.65	—
	0.31	0.59	0.34	—
500°C (after SO ₂ poisoning)	0.3	0.22	—	0.75
	0.25	0.22	0.95	0.65

^a *R*_{CO}, *R*_{HC} = reaction rate of the mixture; (*R*_{CO})^o, (*R*_{HC})^o = reaction rate of each oxidant existing alone under otherwise the same reaction conditions.

controlling should be used for the comparison among the various catalysts as they are less complicated by the interference of the external conditions such as the flow rates used. Some representative rates obtained in this region are listed in Table 5. The variation amounting to twofold among the various samples are not too large in view of the variation existing in the kinetic parameters used to bring the data onto the same basis. The activity of the Co₃O₄ catalysts for CO oxidation exceeds all the other base metal oxides studied in this laboratory. This high activity for Co₃O₄ was also reported by other workers (4, 5). A comparison between the activity over the base metal oxides and that over the noble metal catalysts such as Pt is difficult due to the divergent differences in the kinetic parameters between the two groups. Under the condition as described in Table 5, the activity for CO oxidation at 200°C are comparable over Co₃O₄ and Pt. At lower temperatures, and/or higher concentration of CO the comparison favors Co₃O₄, while higher temperature or lower CO concentration or higher O₂ concentration favors Pt. The presence of H₂O is detrimental to the Co₃O₄ and has little effect on Pt. The Co₃O₄ activity for C₂H₄ oxidation is much inferior to that over Pt.

Oxidation of CO and C₂H₄ Mixtures

At low temperatures, the oxidation of CO is so much faster than that of C₂H₄, so that the effect of CO on the oxidation of C₂H₄ is difficult to measure. On a SO₂ poisoned surface, the retardation of C₂H₄ oxidation by the presence of CO at 500°C was found to

be more severe than the reversed effect on CO oxidation by C₂H₄ (Table 6).

The CO oxidation at 200–250°C was found to be severely retarded by the presence of C₂H₄ even though the oxidation of the latter was negligible at these low temperatures as shown in Table 6 and Fig. 7. Competition between CO and C₂H₄ for the surface sites is most likely the cause of the retardation.

Effect of NO on the Oxidation of CO

As it is shown in Fig. 7, the rate of oxidation of CO at 200°C was retarded by the presence of NO but no reaction of CO with NO was observed. The effect of NO was not carried out at higher temperatures as the interaction of CO and NO is possible at higher temperatures. The retardation of CO oxidation by NO and C₂H₄ was reversible if sufficient time was allowed to remove the

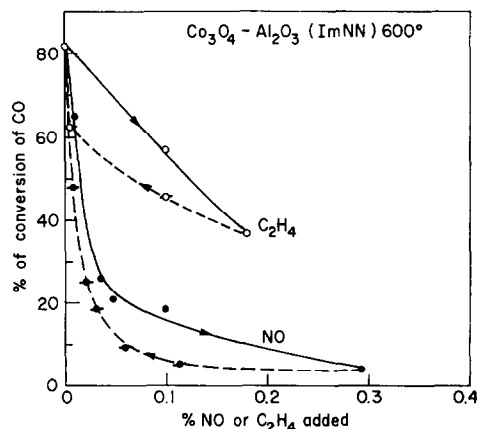


Fig. 7. Effect of NO and C₂H₄ on the rate of CO oxidation over Co₃O₄-Al₂O₃ (ImNN) 600°C, inlet 1% O₂, 1% CO, 0% H₂O. Temperature of oxidation: 200°C.

C₂H₄ and NO from the surface under the reaction conditions.

Effects of SO₂ on the Oxidation of C₂H₄ and CO

SO₂ was introduced into the reacting stream in the form of argon containing 0.1% of SO₂ and the concentration of SO₂ in the reacting mixture was monitored by the concentration of argon. The change of reaction rate as a function of SO₂ introduced into the system are shown in Fig. 8. At 450°C or below, the activity for C₂H₄ oxidation over Co₃O₄ (I) decreased almost linearly with the amount of SO₂ introduced and reached near complete inhibition after about 0.12 ml of SO₂/m² of the catalyst surface was introduced. This amount is of the order of magnitude expected for monolayer coverage for SO₂ on the surface (30 Å²/SO₂) (1). At higher temperatures, a much smaller fraction of the SO₂ introduced was taken up by the surface. At 500°C and above, there was an apparent equilibrium between the degree of poison and the concentration of SO₂ in the gas phase as shown by the step function in Fig. 9. The change of reaction rate or the degree of poison as a function of ppm of SO₂ are shown in Fig. 10. In these plots the rates are at constant inlet concentrations rather than constant average partial pressures of the reactants, therefore, the actual degree of poison would be even greater than it is shown. The oxidation of C₂H₄ was found to be more sus-

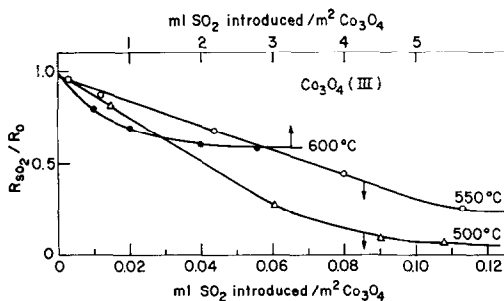


FIG. 8. Effect of SO₂ on rate of C₂H₄ oxidation over Co₃O₄ (III)—600°C. (●) 600°C, inlet concentration 1% O₂, 0.23% C₂H₄, 0.7% H₂O, 6 ppm SO₂. (Δ) 500°C, inlet concentration 1% O₂, 0.17% C₂H₄, 0.6% H₂O, 2.5 ppm SO₂. (○) 550°C, some inlet concentration as 500°C.

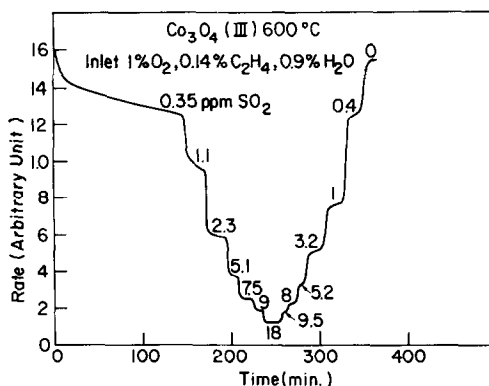


FIG. 9. Effect of SO₂ on rate of C₂H₄ oxidation over Co₃O₄ (III)—600°C as a function of time. Reaction temperature 600°C, inlet concentration 1% O₂, 0.14% C₂H₄, 0.9% H₂O.

ceptible to the SO₂ than for CO, this is contrary to that found over the CuCr₂O₄ catalysts. (3). If the reaction was allowed to continue after the SO₂ source was turned off, some recovery of the activity was observed. The rate and maximum degree of recovery was found to increase with the reaction (regeneration) temperature and increased slightly with increase in partial pressure of water. Some results of the regeneration studies are shown in Table 7. It appears that poison induced at lower temperatures are more difficult to remove than that induced at higher temperatures after being brought to the same regeneration tem-

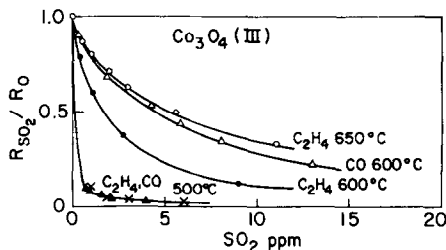


FIG. 10. Rate of CO and C₂H₄ oxidation over Co₃O₄ (III)—850°C as a function of SO₂ concentration. (Δ) CO + O₂ 600°C, inlet: 0.8% O₂, 0.8% CO, 0.7% H₂O, SO₂ varied. (○) C₂H₄ + O₂ 650°C, inlet: 1% O₂, 0.14% C₂H₄, 0.9% H₂O, SO₂ varied. (●) C₂H₄ + O₂ 600°C, inlet: 0.7% O₂, 0.14% C₂H₄, 0.9% H₂O, SO₂ varied. (×) C₂H₄ + O₂ 500°C, inlet: 0.8% O₂, 0.14% C₂H₄, 0.9% H₂O, SO₂ varied. (▲) CO + O₂ 500°C, inlet: 0.8% O₂, 0.8% CO, 0.7% H₂O, SO₂ varied.

TABLE 7
 SO₂ POISON ON CO₃O₄ (I)

Reaction	T _{SO₂} added (°C)	(R _{SO₂} /R _O) _{min} ^a	T regeneration ^b (°C)	(R'/R _O) _{Temp} ^c
C ₂ H ₄ + O ₂	500	0.05	500 (1 hr)	(0.20) ₆₀₀
			↓	
			600	(0.80) ₆₀₀
C ₂ H ₄ + O ₂	600	0.30	600	(1.00) ₆₀₀
				(0.95) ₄₀₀
C ₂ H ₄ + O ₂	400	0.02	400	(0.15) ₄₀₀
			↓	
			600	(0.67) ₄₀₀
CO + O ₂	500	0.05	500 (18 hr)	(0.80) ₆₀₀
	↓		↓	(0.75) ₄₀₀
				(0.60) ₃₅₀
				(0.33) ₃₀₀
	500	0.03	500 (18 hr)	(0.85) ₆₀₀
	↓		↓	(0.60) ₃₅₀
				(0.25) ₃₀₀
	500	0.03	500 (18 hr)	(0.85) ₆₀₀
				(0.30) ₃₀₀

^a (R_{SO₂}/R_O) = rate after SO₂ poisoning/rate before SO₂ poisoning.

^b Temperature reaction continued with SO₂ removed from inlet.

^c (R'/R_O) = rate after regeneration/rate before SO₂ poison.

perature. Since the oxidation of CO and C₂H₄ at these high temperatures over the unpoisoned surfaces were in the diffusion controlling region, the regenerated activity at the high temperatures may not be the true indicator of the extent of the surface covered by SO₂. The activity at 300°C

shows that complete recovery could only be achieved at 600°C or above for SO₂ introduced at 600°C. Furthermore, additional irreversible poisoning could be introduced to the partially poisoned surface by repeated poisoning at 500°C or below. The difference in degree of poisoning (or re-

 TABLE 8
 KINETIC PARAMETERS OF OXIDATIONS OVER THE SUPPORTED CO₃O₄ CATALYSTS^a

Reactant	Temp range (°C)	-l(NS)	m(NS)	n(NS)	f(NS)	ΔE(NS) (kcal/mole)
<i>I. 600°C Samples</i>						
CO	125-200	—	0.44 ± 0.11 (22)	0.47 ± 0.14 (23)	0 (3)	15 ± 1 (13)
CO	250-350	—	0.25 ± 0.1 (16)	0.90 ± 0.13 (16)	~0.5 (2)	3-7 (5)
C ₂ H ₄	300-450	0.4 ± 0.1 (4)	0.26 ± 0.08 (20)	0.39 ± 0.04 (20)	0 (3)	20 ± 2 (11)
C ₂ H ₆	300-450	0.35 ± 0.1 (3)	0.24 ± 0.04 (10)	0.53 ± 0.05 (10)	0 (2)	18.5 ± 1 (6)
<i>II. 850°C Samples</i>						
CO	150	—	0.31 ± 0.07 (17)	0.38 ± 0.11 (17)	—	10 ± 2 (10)
CO	300	—	0.16 ± 0.1 (15)	0.80 ± 0.07 (15)	—	—
C ₂ H ₄	350-450	0.3 ± 0.1 (3)	0.31 ± 0.07 (14)	0.47 ± 0.08 (14)	0 (2)	16 ± 2 (4)
C ₂ H ₆	350-450	—	0.4 (1)	0.48 (1)	—	21 (1)

^a R = k(p_{O₂})^m(p_{CO or HC})ⁿ(p_{H₂O})^le^{-ΔE/RT}. NS = number of runs used for averaging.

TABLE 9
 SPECIFIC RATES OVER SUPPORT Co₃O₄ CATALYSTS^a

Catalyst	Wt% Co ₃ O ₄	CO + O ₂ ^b		C ₂ H ₄ + O ₂ ^d		C ₂ H ₆ + O ₂ ^e
		R _{150°C}	R _{200°C}	R _{350°C}	R _{400°C}	R _{400°C}
<i>I. 600°C Catalysts</i>						
Co ₃ O ₄ -DAL(1)	25.2	90	900	41	102	12
Co ₃ O ₄ -DAL(3)	45	46	530	28	65	—
Co ₃ O ₄ -DAL(4)	10	45	1000	42	102	14
Co ₃ O ₄ -DAL(6)	13.1	75	940	38	122	15.5
Co ₃ O ₄ -DAL(10)	9.8	105	700	29.5	90	—
Co ₃ O ₄ -DAL(11)	8.4	120	600	19	48	—
Co ₃ O ₄ -DAL(13) ^c -600°C	10.1	6.7	20.5	0.1	0.4	—
Co ₃ O ₄ -DAL(13) ^c -850°C (1 day)	10.1	23.5	105	0.5	3.6	—
Co ₃ O ₄ -DAL(13) ^c -850°C (3.5 days)	10.1	21	80	—	3.0	—
Co ₃ O ₄ -Linde A	9.2	140	1000	20	—	—
Co ₃ O ₄ -Linde B	15.4	—	61	6.9	18	—
Co ₃ O ₄ -Mullite	9.1	—	~1	—	1.6	—
Co ₃ O ₄ -Cab-O-Sil	13.3	—	4	—	—	—
Co ₃ O ₄ -Al ₂ O ₃ (k)(ImN)	10.4	—	2	—	0.6	—
Co ₃ O ₄ -Al ₂ O ₃ (ImN1)	17.2	—	0.3	—	0.3	—
Co ₃ O ₄ -Al ₂ O ₃ (ImNN)	3.3	70	180	1.6	8.1	—
Co ₃ O ₄ -Al ₂ O ₃ (ImA)	5.5	12	44	0.6	1.35	—
Co ₃ O ₄ -Al ₂ O ₃ (F)(ImNN)	6.05	60	450	20.5	55	—
<i>II. 850°C Catalysts</i>						
Co ₃ O ₄ -DAL(1)	25.2	33	100	3.2	—	0.8
Co ₃ O ₄ -DAL(3)	45	—	20	1.6	—	—
Co ₃ O ₄ -DAL(6)	10	27	90	1.8	—	0.9
Co ₃ O ₄ -DAL(10)	9.8	17	74	1.3	3.4	—
Co ₃ O ₄ -DAL(11)	8.4	27	91	1.7	4.2	—
Co ₃ O ₄ -Linde A	9.2	—	20	—	—	—
Co ₃ O ₄ -Linde B	15.4	—	~6	—	—	—
Co ₃ O ₄ -Al ₂ O ₃ (ImNN)	17.2	13	40	—	—	—
Co ₃ O ₄ -Al ₂ O ₃ (ImA)	5.5	11	43	0.4	0.05	—

^a Rate in ml CO₂/min-g Co₃O₄.

^b 1% O₂, 1% CO, 0% H₂O.

^c Co₃O₄ III-850°C used as starting material.

^d 1% O₂, 0.1% C₂H₄, 0.1% H₂O.

^e 1% O₂, 0.1% C₂H₆, 0.1% H₂O.

covery) for activity at different temperature may result from the increasing contribution of diffusion control versus surface reaction controlling over the unpoisoned surface with increasing temperature.

Attempts have also been made to study the effect of SO₂ on the activity of an Al₂O₃-supported Co₃O₄ catalysts. The results show that the degree of reduction in activity as a function of ppm of SO₂ in the gas phase and of variation in temperature are quite similar to that observed over the

unsupported Co₃O₄. The total amount of SO₂ introduced into the system to cause near complete poisoning at 400°C was of the order of 5 ml SO₂/g Co₃O₄ which is equivalent to 40 m²/g Co₃O₄ (Fig. 11). This is somewhat higher than that expected from the specific activity of the catalyst (Table 9), but far less than the total surface area of the catalyst. Therefore, the adsorption of SO₂ or SO₃ on the alumina support under the reaction conditions, if it did take place, is of much smaller surface coverage than

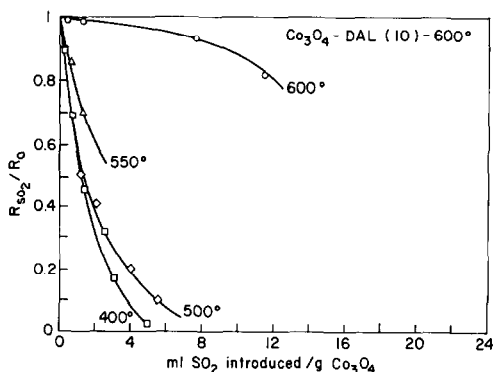


FIG. 11. Effect of SO_2 on rate of C_2H_4 oxidation over Co_3O_4 -DAL (10)-600°C. Inlet: 2% O_2 , 0.5% C_2H_4 , 0.7% H_2O , SO_2 varied.

that of the Co_3O_4 . The possibility of utilizing the alumina support as a scavenger for the SO_2 is thus probably limited.

Kinetics of CO and Hydrocarbons Oxidation over the Supported Catalysts

The general reaction characteristics and their kinetic parameters over the supported Co_3O_4 catalysts are similar to that reported above for the unsupported Co_3O_4 . The average values of l , m , and n and the number of samples used for the averaging are listed in Table 8. Some specific rates of the oxidation reactions over the supported catalysts are listed in Table 9. In view of the complexity of the reactions, the variation of the kinetic parameters, and the interference of the mass transfer problems, the results can only be examined on a semiquantitative basis. Since we do not know the surface area of Co_3O_4 in these catalysts, the results in Table 19 and Figs. 12-14 are expressed in terms of rate of CO_2 formed per gram of Co_3O_4 .

The total surface areas of a few of the Co_3O_4 -DAL series were determined using N_2 adsorption at -195°C . The surface area of the Co_3O_4 particles in the mixed catalysts were estimated to be the arithmetic mean of the surface areas of the starting Co_3O_4 and that (of the respective oxide) after heating at 600 or 850°C. These estimations are arbitrary, but they are acceptable for the purpose of correcting the total surface area measured to give the surface area of

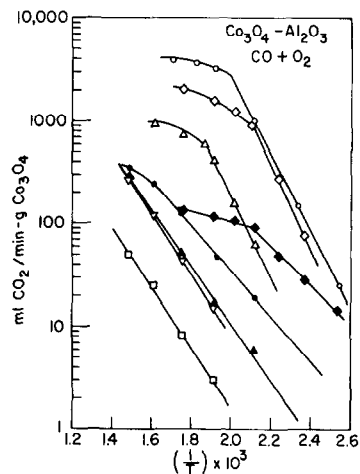


FIG. 12. Arrhenius plots of CO oxidation over mixed Co_3O_4 - Al_2O_3 catalysts. 1% O_2 , 1% CO , 0% H_2O , S.V. $(1-5) \times 10^6 \text{ hr}^{-1}$. \circ Linde A-600°C; \diamond Dispal (b)-600°C; \triangle Linde B-600°C; \blacklozenge Dispal (b)-850°C; ∇ Cab-O-Sil-600°C; \square Mullite-600°C; \bullet Linde A-850°C; \blacktriangle Linde B-850°C.

the alumina particles. The surface areas of the Co_3O_4 and those of the Dispal after being heated separately are included in Table 3. It is shown that the presence of Co_3O_4 as a minor component can inhibit the sintering of the alumina. At high concentration of Co_3O_4 , the sintering of the

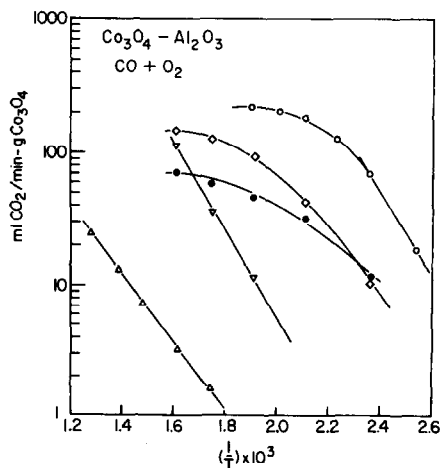


FIG. 13. Arrhenius plot of CO oxidation over impregnated Co_3O_4 - Al_2O_3 catalyst. 1% O_2 , 1% CO , 0% H_2O , S.V. $(1-5) \times 10^6 \text{ hr}^{-1}$. \circ Co_3O_4 - Al_2O_3 (ImNN)-600°C; \diamond Co_3O_4 - Al_2O_3 (ImA)-600°C; \circ Co_3O_4 - Al_2O_3 (ImNN)-850°C; ∇ Co_3O_4 - Al_2O_3 (K) (ImN)-600°C; \triangle Co_3O_4 - Al_2O_3 (ImN)-600°C.

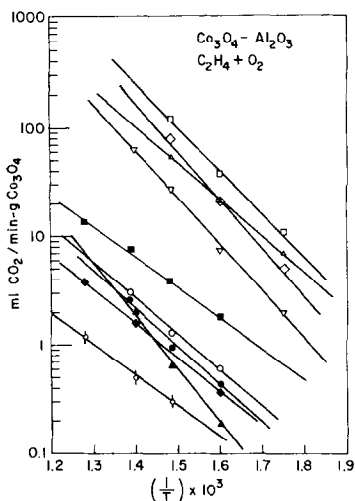


FIG. 14. Arrhenius plots of C₂H₄ oxidation over Al₂O₃ supported Co₃O₄ catalysts. 1% O₂, 0.1% C₂H₄, 0.1% H₂O, S.V. (1-5) × 10⁶ hr⁻¹. ◇ Co₃O₄-Linde A—600°C; △ Co₃O₄-Al₂O₃ (ImNN)—600°C; ▲ Co₃O₄-Al₂O₃ (ImNN)—850°C; ○ Co₃O₄-Al₂O₃ (ImA)—600°C; ● Co₃O₄-Al₂O₃ (ImA)—850°C; □ Co₃O₄-DAL (6)—600°C; ■ Co₃O₄-DAL (6)—850°C; ◆ Co₃O₄-Al₂O₃ (ImNN)—600°C; ♦ Co₃O₄-Mullite—600°C; ∅ Co₃O₄ Al₂O₃ (ImNI)—600°C.

alumina support approaches that of the pure alumina.

The evaluation of the Co₃O₄ surface area in the mixed catalysts is more complex because there is transfer of CO from the Co₃O₄ particles to the support followed by the reaction of some portion of the transferred Co₃O₄ to form the catalytically inactive CoAl₂O₄ in addition to the sintering of the Co₃O₄ particles. The transfer of Co or increasing of Co surface area was shown most clearly in the case of the Co₃O₄-DAL (13) samples. These samples were prepared from Co₃O₄ III—850°C which has been pre-sintered at 850°C to 1.2 m²/g. The results showed that the activity of the 600°C sample was about the same as that of the starting Co₃O₄ III—850°C. But a large increase in activity was observed after heating the sample to 850°C and the time of 1 or 3.5 days made little difference. Since the 850°C heated samples were all blue in color, there was considerable CoAl₂O₄ formation (inactive) in addition to the transfer of some active species (Co₃O₄). Thus, the transfer of Co was very likely much

more than that indicated by the activity increment. The fact that the activity of the Co₃O₄-DAL (1-6) (600°C) samples were of the order of magnitude equivalent of 25-60 m²/g Co₃O₄ compared with the starting surface area of the Co₃O₄ of 24-38 m²/g also suggest the spreading of Co to the support surface.

The Arrhenius plots for the reactions over the 600°C samples are, in most cases, similar to those obtained over the unsupported Co₃O₄ consisting of a linear portion of relatively high activation energies at low temperatures and a nearly flat portion at high temperatures (Figs. 12-14). Over the 850°C samples, the Arrhenius plots are curved over a wide range of temperatures studied. One of the possible explanations of these results is that the fine alumina particles were sintered to form porous cages surrounding the Co₃O₄ phase during heating at high temperatures. Therefore, the reaction over such catalysts would be more likely being impeded by the rate of diffusion in and out of the pores. This mass transfer effect makes it very difficult to evaluate the results over the 850°C samples. Qualitatively one can conclude that the alumina supported Co₃O₄ deactivated badly after heating at 850°C. The deactivation resulted from (1) sintering of the Co₃O₄ particles, (2) sintering of the alumina support to a mass transfer barrier, and (3) reaction to form the inactive CoAl₂O₄. It also appears that the deactivation is worse for the C₂H₄ oxidation than for CO. Since the two reactions were studied at different temperature range, the mass transfer effect may have played a role in causing this difference also.

The results show that the activity of the catalysts formed as a mechanical mixture is much greater than those prepared by impregnation. For the latter, the close contact between the support surface and a layer of Co salt of a few angstroms thick may facilitate the reaction to form CoAl₂O₄ and to deactivate the catalyst severely. The catalyst prepared by impregnation in the acetate solution was far better than that from the nitrate solution. The stronger acidity of the cobalt nitrate may have attacked the alumina to form Al(NO₃)₃ which may play

a role in the deactivation of the Co_3O_4 formed on calcination. The reason for the difference between the Kaiser alumina and the dried Dispal is not known. If the Co was precipitated out by a stream of NH_3 immediately after impregnation and the NH_4NO_3 removed at 150°C prior to heating, the activity of the resulted catalyst was much higher. The NH_3 -treated catalysts are probably a fine mixture of Co_3O_4 and Al_2O_3 such as the Co_3O_4 -DAL mechanical mixture catalysts rather than a Co salt-coated Al_2O_3 surface as expected for a truly impregnated catalyst.

It is surprising to find the large difference among the mechanical mixture catalysts formed from the same Co_3O_4 starting material with different inert diluents. The activity decreases in the order: Linde A (α -alumina) > Linde B (γ -alumina) > Cab-O-Sil (colloidal SiO_2) > mullite (aluminum silicate). Presumably, the ease of reaction between Co and the support to

form the inactive aluminate and silicate increases in the same order.

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