Kinetics of CO Oxidation over $Co_3O_4/\gamma\text{-}Al_2O_3$

Part III: Mechanism

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Interpretations of a variety of transient experiments are combined with information from the literature to reveal the roles played by the Co_3O_4 catalyst surface and adsorbed species. The reaction path depends on the oxidation state of the catalyst. A rather coherent picture of oxidation-reduction catalysis by a metal oxide is obtained.

SCOPE

The mechanism of oxidation-reduction reactions on metal oxide catalysts is not well understood. In particular, very little coherence exists in the information available on the very active catalyst for CO oxidation, Co_3O_4. It is believed that the trivalent cobalt ion in the spinel structure is responsible for CO oxidation. However, the roles of lattice oxygen and various adsorbed species are not at all clear. Steady state and unsteady state kinetic studies were reported in the previous papers (Parts I and II). The dynamic studies provided a wealth of phenomenological insights that can be used to postulate a mechanism for this catalytic reaction. The postulated mechanism can then be checked for consistency with the rate equation from the steady state studies and with information from the fragmented literature. The mechanism thus postulated and evaluated may promote practical exploitation of this catalytic reaction, provide insight into the general matter of metal oxide catalysis, and suggest productive avenues for future research.

CONCLUSIONS AND SIGNIFICANCE

The phenomenological conclusions from the reactor dynamics studies (Part II) and specific chemical information from the literature provided the basis for the postulation of a mechanism for the oxidation of CO over $Co_3O_4/\gamma\text{-}Al_2O_3$. The reaction path depends in a number of ways on the oxidation state of the catalyst. From the mechanism a rate equation can be derived for the circumstances of the steady state experiments. Excellent agreement is found between this rate equation and the one obtained in Part I. This provides partial validation of the postulated mechanism. The mechanistic insights also suggest the origins of the two kinds of catalyst deactivation contemplated in Part I. Finally, a rather coherent picture of oxidation-reduction catalysis by a metal oxide is obtained.

INTRODUCTION

Mechanisms of metal oxide catalyzed reactions are much less well understood than for supported metal catalysts. Some qualitative reaction mechanisms for CO oxidation over cobalt oxide and other metal oxides in general have been put forth by Dwyer (1972), Hofer et al. (1964), Krylov (1970), Boreskov (1973), Klissurski et al. (1970), and Hertl (1973). Kobayashi and Kobayashi (1976) proposed and evaluated, somewhat more quantitatively, a mechanism for CO oxidation on $\alpha\text{-}Cr_2O_3$. It is known that the reaction mechanism varies from one oxide catalyst to another and from

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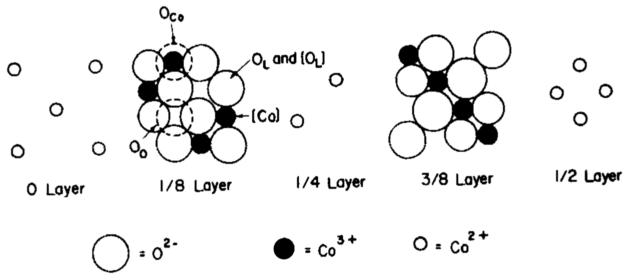


Figure 1. (100) plane of Co_3O_4 spinel $[Co^{2+}]^{IV[Co3+]}{}_2^{VI}[O^{2-}]_4$.

temperature to temperature (Boreskov, 1973; Margolis, 1973). In addition to defining better the general mechanism for metal oxide catalysis, it would be desirable to explain the exceptional activity of Co_3O_4.

In the present work the oxidation of carbon monoxide over supported cobalt oxide was studied by both dynamic and conventional steady state experiments. The results of the dynamic studies defined the kinds of phenomena that occur and suggested the kinds of sites that must be involved. Prompted by the literature, this paper attempts to add specific chemistry to the deductions of Part II and the quantitative kinetics of Part I to produce a catalytic reaction mechanism that is consistent with all available information. Of course the risk of overgeneralization is great. The proposed mechanism, even if correct, need not be the only one. Furthermore, the steps proposed may not be the most elementary ones. Nevertheless, as Durant and Durant (1968) said, "We proceed."

CATALYTIC SURFACE AND ACTIVE SITES

No meaningful reaction mechanism can be postulated unless the surface sites responsible for the formation and reaction of the various adsorbed species can be identified. Considerable progress has been made to characterize the surfaces of supported metal catalysts. The task is much more difficult for supported metal oxide catalysts. Even though most pure metal oxides exhibit well-defined crystalline structures, such crystallinity may not exist on a support except in large metal oxide particles. Even for well-defined crystals, the surface contains many crystallographic planes. A simplified picture of Co_3O_4 is invoked here to identify the catalytically active sites, implied by the experimental observations and deductions presented in Part II. Such an approach, while not rigorous, provides considerable insight into the possible role played by the surface of this catalyst in CO oxidation.

Crystalline Co_3O_4, $[Co^{2+}]^{IV}[Co^{3+}]_2^{VI}[O^{2-}]_4$, is a normal spinel formed by cubic close packing of oxygen anions with trivalent and divalent cobalt cations located in the octahedral and tetrahedral spacings within and between anion layers. A unit cell of Co_3O_4 contains 32 oxygen anions. Eight of a possible 64 tetrahedral locations between anion layers are filled by Co^{2+}, while 16 out of a possible 32 octahedral locations within anion layers are filled by Co^{3+} (Fyfe, 1964).

Figure 1 shows various parallel planes that can be obtained in the [100] direction if a unit cell of Co_3O_4 is sectioned at various locations (Yao and Shelef, 1974). If it is assumed that the crystallites on the support are cubic in shape, the catalyst surface would consist of equivalent planes of the type (100), (010), and (001).

Krylov (1970), Boreskov (1973), Yao and Shelef (1974), and Carette and Bonnelle (1977) have shown that the trivalent cobalt ion in cobalt oxide is responsible for oxidation reactions. Thus the surfaces that include Co^{3+} must be the catalytically active ones. In Figure 1, these would correspond to the $\frac{1}{8}$ and $\frac{3}{8}$ layers in the [100] direction.

Upon examining the $\frac{1}{8}$ and $\frac{3}{8}$ layers, one can easily assign two distinct sites according to the surface features. The trivalent cobalt ion on the surface comprises one type of site and is designated [Co]. The other site is formed by the lattice oxygen and is designated $[O_L]$. Sites [Co] and $[O_L]$, thus envisioned, are shown in Figure 1. In addition, a third site can be visualized as a vacancy, $\square_L$, generated by the removal of a lattice oxygen.

FORMS OF SURFACE OXYGEN

The dynamic experiments (see Table 2, Part II) suggested three distinct forms of surface oxygen. These oxygen forms are taken to be lattice oxygen, O_L, oxygen adsorbed on trivalent cobalt, O_{Co}, and oxygen adsorbed on lattice oxygen O_O. In Figure 1, the lattice oxygen, O_L, is seen to be the reaction site, $[O_L]$. The oxygen adsorbed on the trivalent cobalt, O_{Co}, can be envisioned as completing the octahedron around the Co^{3+}. The oxygen adsorbed on lattice oxygen, O_O, can be imagined to be located on an octahedral spacing in the surface which is unoccupied. Dashed circles in Figure 1 designate O_O and O_{Co}.

The presence of three distinct oxygen forms on the surface of Co_3O_4 has also been reported by Halpern and Germain (1975). They carried out thermodesorption studies on a single pellet of Co_3O_4, which was "cleaned" by evacuating the chamber containing the pellet to 10^{-6} torr at 773–973 K. Prior to the desorption run, the pellet was exposed to pure O_2 at a pressure of 200 torr at 773 K. Excess O_2 was condensed by cooling below 223 K. Their subsequent thermodesorption studies showed three distinct oxygen peaks on the spectrogram at temperatures of 390, 575, and 710 K. Halpern and Germain concluded that at least three different states of surface oxygen can exist on a Co_3O_4 surface. They speculated that these oxygen forms can be associated with chemisorbed and lattice oxygen. However, they cautioned that a clear-cut distinction between adsorbed and lattice oxygen is often difficult and that interconversion between the two is probable.

Sazanov et al. (1968a,b) also studied the adsorption of oxygen on the surface of Co_3O_4. They found that the heat of adsorption increases as the surface coverage of oxygen decreases. Their plot of heat of adsorption vs. surface coverage yielded an inflection point in the curve, which implies a distinct inhomogeneity of the surface. Such a behavior can be explained if more than one form of surface oxygen is present.

The surface-to-oxygen bond energies for the postulated surface oxygen species may be in the following decreasing order, $O_L > O_{Co} > O_O$. If lattice oxygen vacancies exist, oxygen would tend to fill the vacancies in preference to adsorbing on Co^{3+}. If no surface vacancy exists, the tendency for the formation of O_{Co} should be greater than O_O. This would occur because any Co^{3+} ions on the surface would have unsaturated valencies and would prefer to complete the anionic octahedra surrounding them (Krylov, 1970). Formation of O_O can hardly be strongly bonded because of anionic repulsion, and its formation can only be justified by some kind of charge stabilization.

These are essentially thermodynamic arguments. It would be convenient if activation energies for formation of these oxygen species followed in the reverse order: i.e., $O_O > O_{Co} > O_L$. Then both kinetic and thermodynamic factors would suggest the same relative rate dependencies. Intuitively, however, if seems more likely that the uptake of the more weakly bound oxygen, O_O, would require the least activation. Halpern and Germain (1975) give activation energies of 84, 150, and 210 kJ/mol for the desorption from Co_3O_4 of oxygen in three distinct states. Unfortunately they were unable to link unambiguously the three states to identifiable surface species. The apparent conflict of rate-determining factors is consistent with the observations that no single rate-determining step is wholly dominant, that several paths for the reaction coexist,

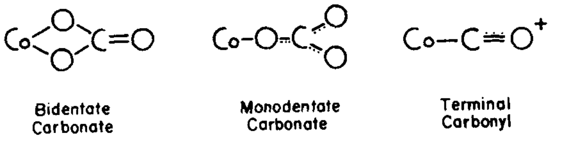


Figure 2. Forms of adsorbed CO and CO_2.

and that reaction behavior is altered markedly by conditions.

No speculation will be made regarding the detailed ionic nature of these surface oxygen species. Surface oxygen, however, is known to exhibit various ionic forms over supported metal oxide catalysts. Lunsford (1973) has reviewed the research on electron spin spectroscopy of adsorbed oxygen species on oxide catalysts. The presence of O^-, O_2^-, and O_3^- species has been firmly established.

REACTION MECHANISM

The proposed reaction mechanism can be stated as
Reaction steps for steady state conditions:

$$1/2O_2 + [Co] \xrightarrow{\text{slow}} [Co]\cdot O_{Co} \qquad \text{Step 1}$$

$$[Co]\cdot O_{Co} + CO + [O_L] \rightarrow [Co] + [O_L]\cdot CO_2 \qquad \text{Step 2}$$

$$[O_L]\cdot CO_2 \rightleftarrows [O_L] + CO_2 \qquad \text{Step 3}$$

Additional steps for prolonged oxidation and subsequent reaction:

$$[O_L] + 1/2O_2 \rightarrow [O_L]\cdot O_O \qquad \text{Step 4}$$

$$2[O_L]\cdot O_O + CO \rightarrow 1/2O_2 + [O_L]\cdot CO_2 + [O_L] \qquad \text{Step 5}$$

Additional steps for prolonged reduction and subsequent reaction:

$$[O_L] + CO \rightarrow \square_L + CO_2 \qquad \text{Step 6}$$

$$\square_L + CO + O_2 \rightarrow [O_L] + CO_2 \qquad \text{Step 7}$$

Steps 1 to 3 represent the mechanism by which the reaction proceeds at the steady state conditions in Part I. If the catalyst is exposed to oxygen for a prolonged period of time, additional adsorption of oxygen, as represented by step 4, can take place. If such an oxidized catalyst is brought into contact with carbon monoxide, the reaction can proceed via steps 5 and 3, as well as by steps 1 to 3. Reduction of the surface by CO can be represented by step 6. Carbon dioxide is produced in the process. The reoxidation of a reduced surface produces CO_2 via step 7 concomitantly with CO_2 production by steps 1 to 3.

Reaction at Steady State Conditions

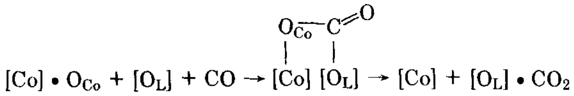
Steps 1 to 3 describe the path by which the reaction occurs at steady state. It is concluded that adsorbed oxygen, O_{Co}, reacts with the gaseous CO to form an adsorbed species of CO_2 on a neighboring site $[O_L]$. The adsorbed CO_2 then desorbs to produce gaseous CO_2.

The reasons for choosing O_{Co} as the oxygen responsible for reaction are many. Boreskov (1973) has concluded that CO oxidation at 488 K must be mainly proceeding by a concerted mechanism. He arrived at this conclusion by comparing the rates of the surface reduction and oxidation with the rates of CO oxidation for various metal oxide catalysts, including cobalt oxide. He found that surface reduction rates below 573 K are much slower than the rates of CO oxidation. Thus participation of the lattice oxygen at lower temperatures in CO oxidation is unlikely.

The results presented in Part II show that regeneration of surface oxygen is the slowest step among steps 1 to 3. If the lattice oxygen were responsible for the reaction, thermodynamics suggests a relatively easy regeneration because of the high lattice energy of O_L. If a large activation energy precluded this, then a similarly large activation energy might make the reaction of CO much slower with lattice oxygen than with adsorbed oxygen.

Hertl (1973) and Goodsel (1973) have shown with *in situ* infrared studies that upon introduction of CO over cobalt oxide, bidentate or monodentate carbonate species are formed on the surface. Adsorption of CO_2 also leads to similar carbonate species. These species are quite stable and are detectable up to 500 K. Only upon a reduced catalyst does CO form a carbonyl type of bond in which a cobalt to carbon bond exists. The structures of these three species are shown in Figure 2. It can be visualized from these structures that lattice oxygen must be the site for the adsorption of CO_2 to form a carbonate species. However, the additional oxygen required when CO is oxidized to CO_2 must have been picked up from a neighboring site, O_{Co} or another O_L.

Step 2 in the reaction mechanism implies that two neighboring sites, [Co] and $[O_L]$, are involved in formation and subsequent desorption of CO_2. The species $[O_L]\cdot CO_2$ can be identified as monodentate carbonate shown in Figure 2. Step 2 might proceed via an intermediate step in which the bidentate carbonate is formed. This can be shown as:



$$[Co]\bullet O_{Co} + [O_L] + CO \rightarrow \overset{O_{Co}-C{=}O}{[Co]\ [O_L]} \rightarrow [Co] + [O_L]\bullet CO_2$$

However, no experimental evidence exists in this research to justify such a sequence.

Step 3 indicates reversible adsorption of CO_2 on site $[O_L]$. Experimental results presented in Part II indicate that CO_2 does adsorb reversibly on the catalyst. Furthermore, it was found that the presence of oxygen did not affect the amount of CO_2 adsorbed. This fact supports assignment of $[O_L]$ sites for CO_2 adsorption, leaving [Co] sites free for adsorption of oxygen. It was also found experimentally that addition of CO_2 during the reaction affected the conversion very mildly. This fact can also be accounted for by the proposed mechanism in that reversible adsorption of CO_2 can occur independently from the reaction.

The proposed mechanism also explains the role played by CO. In Part II it was shown that if a step decrease in CO or in both CO and O_2 is imposed in the feed, the CO_2 responses at the reactor outlet are found to be identical. From the proposed mechanism it is obvious that adsorbed CO_2 is the only source of CO_2 after CO is removed from the gas phase. This adsorbed CO_2 desorbs in the same manner whether or not oxygen is present in the gas stream. It also shows that if any reversible CO adsorption is occurring, the adsorbed CO is not responsible for reaction. Otherwise, in the presence of oxygen, CO_2 formation would have given more CO_2 in the response. Hertl (1973) found that heating a sample of Co_3O_4, preadsorbed with CO, yielded only CO_2. This implies that CO interacts with the catalyst only by reaction with surface oxygen. Furthermore, this shows that step 2 is irreversible.

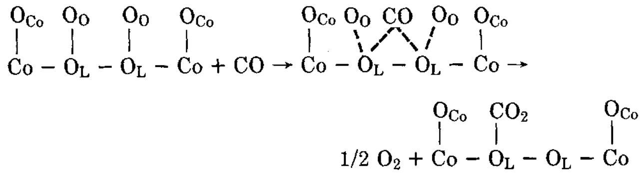
During the course of the steady state experiments, described in Part I, it was observed upon changing the partial pressure of CO at constant partial pressure of O_2 that the new steady state was achieved much faster than when P_{O_2} was changed at constant P_{CO}. This can be explained by the proposed reaction mechanism. Since no CO is adsorbed on the surface, a change in CO partial pressure affects only the gas phase concentration. Thus a new steady state would be established rapidly. Upon changing P_{O_2}, however, step 1 would have to readjust until the concentration of $[Co]\cdot O_{Co}$ achieves its new steady state. Because this step is the slowest, the establishment of a new steady state would occur slowly.

Finally, speculation can be made regarding the long-term decline of the catalytic activity that was observed during the steady state kinetic studies. Such an effect might be attributed to a very slow formation of a stable bidentate carbonate species, which would keep sites $[O_L]$ and $[Co]$ from participation in steps 2 and 1, respectively. Klissurski (1974) found by temperature-programmed desorption studies that stable adsorbed CO_2 can exist up to 653 K. An alternate explanation of the activity decline will be presented shortly.

Prolonged Oxidation and Subsequent Reaction

Step 4 in the proposed reaction mechanism indicates how, under prolonged oxidation, additional surface oxygen, O_O, might form. The results of experiments 3, 4, and 5 reported in Part II are evidence of the formation of this species. Formation of weakly bound O_O is taken to be a step with low bond energy. At the temperature of this study, it is suspected that its formation occurs only after all of the lattice vacancies are filled and oxygen has adsorbed on all Co^{3+} sites to produce O_{Co}. The formation of O_O can be imagined as an additional layer of oxygen residing on top of the 1/8 or 3/8 plane in [100] direction shown in Figure 1.

Step 5 indicates what happens when a surface containing O_O is exposed to CO (a situation corresponding to experiments 4 and 5 in Part II). As CO approaches the surface, it encounters the O_O layer. Due to the interaction of CO with O_L, part of the O_O is released while another part reacts to form the adsorbed carbonate species $[O_L]\cdot CO_2$. The following simplified sequence can be imagined to occur:



Step 4, followed by the sequence shown above, explains the appearance of oxygen in dynamic experiments 4 and 5. The need for step 5 to open up $[O_L]$ sites before step 2 can occur explains the delays in the appearance of the CO_2 maxima (see Figure 3, Part II). Step 5 is rapid and essentially irreversible. Thus, with both O_2 and CO in the gas phase, step 5 would continue until all O_O is liberated or reacted. After that, the reaction would proceed via steps 1 to 3.

In dynamic experiments 3, 4, and 5, the oxygen pretreatment was done at a low O_2 concentration of 0.49 mol/m^3. It is evident that 1 h of such pretreatment is not sufficient to form any observable O_O and it might not even form all possible O_{Co}. However all O_{Co} and some O_O are formed in 16 h of pretreatment. The surface probably becomes saturated with oxygen sometime between 16 and 66 h of pretreatment. It would be interesting to note whether an increase in oxygen concentration during pretreatment would affect these deductions.

Prolonged Reduction and Subsequent Reaction

Step 6 of the proposed reaction mechanism indicates the manner in which CO might react with lattice oxygen, O_L, to form CO_2. It is possible that CO could react with lattice and adsorbed oxygen in parallel. The lattice oxygen is, however, more strongly bonded to the surface and therefore it may react much more slowly with CO than adsorbed oxygen. The continuing formation of small amounts of CO_2 after 15 h in dynamic experiment 5 indicates the reaction of lattice oxygen because no oxygen was fed in that experiment.

Step 7 is indirectly based on the results of experiment 22 described in Part II (see, for example, Figure 8). Upon introducing oxygen to a catalyst, reduced for a period of 0.5 h in the presence of CO, an almost instantaneous CO_2 response occurs, which then slowly declines. If the reaction proceeds only by steps 1 to 3 and if step 1 is the slowest, the CO_2 response should increase slowly. That is, at first O_{Co} would have to be regenerated before reaction could proceed. It is, therefore, concluded that after introducing O_2 onto the reduced catalyst, the oxidation of CO must be proceeding also via step 7. The 0.5 h reduction must have reduced some of the surface and created vacancies. This is possible because no oxygen pretreatment was involved during experiment 22 and there must have been very little O_{Co} or O_O present when the 0.5 h reduction was started. Upon the introduction of oxygen, the vacancies, $\square_L$, appear to fill up quickly, presumably because of the high lattice energy of O_L and a low activation energy. It is possible that such a process might dissociate O_2 to form some active (ionic or radical) atomic oxygen species that then reacts with CO directly to form CO_2. Thus a sequence, as shown below, can be visualized to constitute step 7:

$$\square_L + O_2 \rightarrow [O_L] + O$$

$$O + CO \rightarrow CO_2$$

This energetic sequence could well provide the observed high rate of formation of CO_2 as long as vacancies remained.

In Part II, is was shown that the amount of CO_2 adsorbed on a reduced catalyst is significantly lower than on an oxidized catalyst. If CO_2 is assumed to adsorb on lattice oxygen, as in the postulated mechanism, such a behavior would be expected when vacancies exist.

It would be interesting to know to what extent the catalyst can be reduced by carbon monoxide. From consideration of free energies of formation, the reaction $Co_3O_4 + CO \rightarrow 3CoO + CO_2$ is feasible and at 500 K has $\Delta F = -1.509 \times 10^5$ J/mol (Coughlin, 1954). However, such a reaction may not go to completion because of rate limitations. The diffusion barriers for oxygen within crystals are definitely quite high. This would not prevent the surface from being reduced though.

In the unsteady state experiments the amount of the catalyst used was 18.69 g and the catalyst loading was 6.851 g Co_3O_4/100 g γ-Al_2O_3. Thus the total available oxygen in Co_3O_4 can be calculated to be 5×10^{-3} g-atom. The total amount of CO_2 formed in dynamic experiment 5 by interaction of CO with oxidized catalyst was 4.5×10^{-4} mol. It was discussed earlier that this quantity was presumed to be formed from adsorbed oxygen only. Even if all of this quality were formed by reaction of CO with lattice oxygen, the catalyst would still be an order of magnitude away from complete bulk reduction to CoO after 5 h of exposure to CO. A more exact determination of the number of adsorbed (O_{Co} and O_O) and lattice (O_L) oxygens at the surface is difficult because the particle sizes of the Co_3O_4 crystallites are not known.

The problem of bulk reduction of Co_3O_4 to CoO can also be approached from the other side. Can CoO be oxidized to Co_3O_4 easily? Surprisingly, more work has been done in this direction. However, there are conflicting opinions. Nowotny and Ziolkowski (1977) have summarized the results of previous workers. Their own work showed that there is some incorporation of oxygen into CoO even at room temperature, although the rate of this process is slow. Above 623 K, the rate increases rapidly and about 4% of the cobalt exists in a distinct Co_3O_4 phase. This was found by using x-ray and electron paramagnetic resonance methods. On the other hand, Colaitis et al. (1971) reported that at 503 K, CoO having a particle size of 6×10^{-9} m can be totally oxidized to Co_3O_4 in 60 h. The extent of oxidation decreased as the particle size increased. The evidence is conflicting on the $Co_3O_4 \rightleftarrows CoO$ transformation, but there is no doubt that it can occur. Because CoO is known to be inactive for CO oxidation it is strongly recommended that future work be carried out on this transformation.

This may well be the key to the catalyst deactivation observed in the steady state studies (see Fig. 2, Part I). That is, the reduction of Co_3O_4 by the reaction of CO with lattice oxygen, O_L, may occur at the same time as CO is being oxidized by oxygen adsorbed on trivalent cobalt, O_{Co}. The removal of one divalent lattice oxygen can be expected to reduce two nearby trivalent cobalt ions to the inactive divalent form. Thus the reduction process is amplified by a factor of 2 in its impact on the number of active cobalt sites. Actually step 6 of the postulated mechanism accounts for this catalyst reduction. Thus the conceptual basis already exists for a quantitative model of the catalyst dynamics. Modeling to correlate the data of Figures 2 and 3 in Part I is underway.

There is further evidence for this mechanism of catalyst deactivation. Mehandjiev and Nikolova-Zhecheva (1980) used magnetic susceptibility measurements to show that during CO oxidation at temperatures above 250°C octahedral Co^{3+} ions were either transformed into a high spin state or reduced to octahedral Co^{2+}. At reaction temperatures below 180°C they found no such effect. They make no mention of the duration of their experiments. Our work (at 215°C) is exactly at the midpoint of their minimum high temperature and maximum low temperature. Probably the deactivation we observed (Figure 2, Part I) was much slower than what they detected in their high temperature experiments. Thus their work and ours are consistent within our limits of assessment, and the reduction of Co_3O_4 appears to be the probable cause of our observed catalyst deactivation.

A slightly different, but related, explanation for the curvature in the x_{CO} vs. W/F_{CO} plots of Part I can now be attempted. Mehandjiev and Nikolova-Zhecheva found that about 3% of the Co^{3+} ions underwent the transition described above. Yet they noted that for an ideal spinel only about 0.3% of the Co^{3+} ions are on the surface. Thus they concluded that the changes resulting from the catalytic reaction can penetrate about 10 atomic layers, i.e., well into the bulk of the catalyst. This means that even (perhaps especially) at very low conversions there could be profound changes in the nature of the surface sites. Further the changes may be of such consequence that less accessible sites assume the burden of catalytic action. The effect of this would be to lower the effective number of sites per unit mass of catalyst, thus producing the concave downward curvature in the x_{CO} vs. W/F_{CO} plots of Part I.

COHERENCE OF STEADY STATE AND DYNAMIC RESULTS

The mechanism that has just been presented and discussed is based on the dynamic experiments of Part II. In Part I a rate equation was obtained for time-invariant conditions (steady state). The coherence of these two independent results is a measure of the validity of the research.

A steady state rate expression based on steps 1 to 3 can be derived by assuming step 3 to be in equilibrium and the rates of formation and consumption of O_{Co} to be equal:

$$r = \frac{k_1 k_2 K_3 P_{CO} P_{O_2}^{1/2}}{k_1(K_3 + P_{CO_2}) P_{O_2}^{1/2} + k_2 K_3 P_{CO}} \tag{1}$$

The initial rate expression with $P_{CO_2} = 0$ is

$$r_o = \frac{k_1 k_2 P_{CO} P_{O_2}^{1/2}}{k_1 P_{O_2}^{1/2} + k_2 P_{CO}} \tag{2}$$

If step 1 is rate controlling, $k_1 P_{O_2}^{1/2} \ll k_2 P_{CO}$ and Eq. 2 reduces to

$$r_o = k_1 P_{O_2}^{1/2} \tag{3}$$

Equation 3 is similar in functional form to Eq. 8 of Part I, which was obtained from the steady state experiments. If the steady state data are correlated with Eq. 2, the result is

$$r_o = \frac{4 \times 10^{-8}\, P_{CO} P_{O_2}^{1/2}}{1 \times 10^{-4}\, P_{O_2}^{1/2} + 4 \times 10^{-4}\, P_{CO}} \tag{4}$$

For the values of P_{O_2} and P_{CO} used experimentally, the first term in the denominator ranges from one-half to one-twentieth of the second term. The minor contribution of the $k_1 P_{O_2}^{1/2}$ term explains the observed order of oxygen of 0.41 as compared to the 0.5 of Eq. 3 and accounts for the hint of CO dependence to be found by close examination of Figure 6 of Part I. Equation 4 cannot, however, account for the curvature in the x_{CO} vs. W/F_{CO} data in Part I.

From Eq. 4 one can predict that the use of substantially higher P_{O_2} or lower P_{CO} would cause the reaction rate to become dependent on P_{CO}. Since CO oxidation appears to occur via competitive mechanisms of reaction of CO with adsorbed and lattice oxygen, it may be expected that the relative rates of the two reactions would be affected by temperature. Most evidence points to increasing catalyst reduction with increasing temperature. Also, although adsorption rates increase with temperature, equilibrium adsorption generally decreases. Hence a smaller proportion of CO reacting with adsorbed oxygen can be predicted at higher temperatures.

The question arises as to what makes Co_3O_4 different and more active than other metal oxide catalysts. The probable cause is the availability for reaction of adsorbed O_{Co} on the surface. The $[Co]\cdot O_{Co}$ bond energy appears to be smaller than corresponding metal to adsorbed oxygen bond energies in other 3d metal oxides. An indication of this is cited by Halpern and Germain (1975) wherein standard heats of oxygen desorption are given. Co_3O_4 had the lowest value among TiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3, NiO, CuO, and ZnO. This thermodynamic result is consistent with the observed relative rates of CO oxidation among metal oxides. Presumably, also, the activation energies are lower for oxygen adsorption and reaction on Co^{3+} sites than for the corresponding processes in the crystal lattice. If the $[Co]\cdot O_{Co}$ bond strength were comparable to that of lattice oxygen, either O_{Co} or O_L could have been responsible for the reaction. Furthermore, the scission of the $[Co]\cdot O_{Co}$ bonds (step 2) would have become more difficult than the regeneration of adsorbed or lattice oxygen (step 1 or 7). These circumstances may be more characteristic of other metal oxides. In such cases P_{CO} would exert influence on the reaction rate. For Co_3O_4, however, the reaction proceeds via steps 1 to 3 of the proposed mechanism.

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