Carbon Monoxide Oxidation on Nickel Oxide

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The oxidation of carbon monoxide over nickel oxide has been studied at 160–180°C for partial pressures of CO in the order of 33 Torr. Gases tagged with ^{13}C and ^{18}O have been used to obtain insight concerning the sequence of steps in the reaction. Apparently CO is oxidized in two ways: The reaction of CO(g) with adsorbed oxygen leading to CO_2(g); and the reaction of CO(g) with adsorbed CO_2 to form a two-carbon intermediate, which then is further oxidized to $2CO_2$(g).

INTRODUCTION

In this study we employed the same NiO on silica catalyst that was used for earlier work on the decomposition of N_2O (*1*). By now studying the more complicated CO oxidation reaction and, in the future, other oxidation reactions on this same catalyst, we hope to obtain more information on the sequences of steps involved than might be possible if only one reaction were studied. A quantitative description of the sequence of steps for the N_2O decomposition was obtained by simple experiments involving a step change in the continuous feed to a gradientless reactor from inert gas to a mixture containing N_2O; the only apparent kinetically significant adsorbed species was O^-. However, for CO oxidation, we find, as elucidated later in this paper, that there seem to be three kinds of sites for adsorbed CO_2 in addition to adsorbed oxygen. To find out what is going on we have turned to the use of stable isotopes; work is also in progress using infrared spectroscopy.

In preliminary work it was ascertained that the silica support was not a catalyst for the oxidation of CO at 180°C and that

neither CO, O_2, nor CO_2 was appreciably adsorbed on the support. The literature (*2,3*) indicates that CO_2 does not chemisorb on silica at 180°C, so we expected no exchange between oxygen-18 in CO_2 and oxygen-16 from the support. However, our silica did exchange ^{18}O with CO_2; CO_2 tagged with ^{13}C did not exchange, nor did CO or O_2. The exchange persisted with another pure silica (Davison grade 62) and was not influenced by the presence or absence of water vapor in the gas feed. The exchange may be caused by small amounts of impurities in the silica (*4*).

Since the exchange made it difficult to interpret some of our results, certain experiments were done using unsupported NiO made by decomposing nickel formate in 10% O_2 in helium at temperatures slowly increased to 300°C; the supported catalyst had been treated in the same way. Some characteristics of the catalysts are given in Table 1.

The results given in this study are largely qualitative but indicate quite strongly the probable sequence of steps for CO oxidation on NiO. We are pursuing other transient and steady-state experiments to find the values of the parameters (preexponential factor, activation energy,

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TABLE 1
MATERIALS

Material	Description
NiO on silica	14 wt NiO on Houdry SiO_2; 6.45 g of 1-mm particles; crystallite size 190 Å, i.e., 4.94 m² of NiO/g of supported catalyst; BET surface, 350 m²/g of supported catalyst. Made by impregnation of SiO_2 by a solution of nickel formate and decomposition in 10% O_2 in helium at temperatures slowly increased to 300°C
SiO_2(I)	Houdry macroporous beads
NiO catalyst	1 g of fine particles; BET surface, 61 m²/g. Made by decomposing nickel formate as described above
Davison silica	Grade 62, 60–70 mesh, washed in triply distilled water
$C^{18}O_2$ or CO_2**	93.6%, Miles Laboratories
$C^{18}O$ or CO*	Made from 93.6% CO_2** by exposure to pure carbon at 900°C
^{13}CO or C*O	90.5%, Merck
$^{13}CO_2$ or $C*O_2$	91%, Merck
$^{18}O_2$ or O_2**	99.89%, Miles Laboratories
Helium	99.995%
CO	99.86%
O_2	99.6%
CO_2	99.8%

coverage, sites available, adsorption coefficients etc.) that describe the rates of the steps in the sequence.

EXPERIMENTAL DETAILS

The work using NiO on silica was done in a gradientless reactor (5) with a magnetically driven impeller to assure good mixing. This reactor operates as a continuous-flow, stirred-tank reactor. Since spatial variations in temperature and pressure are suppressed by the good mixing, pulse and other transient experiments are easier to interpret quantitatively than in integral fixed-bed reactors. The void volume of the reactor was 26.45 ml. The studies on adsorption were done with the flow system described previously (1,5); a four-way switching valve was used to change the feed to the reactor from helium to a mixture of reactant(s) plus helium and then, usually after 6 min, back to helium. For the isotope work, a pulse concentration signal was generated by a gas-sampling valve installed in the feed line to the reactor. The isotopic pulse studies using NiO were done on 1 g of sample contained in a glass reactor.

For all pulse experiments, the loop of the gas-sampling valve had a total volume of 2.21 ml; the various gases were admitted to this loop always at a pressure of 100 Torr, so that the gas sample was equivalent to 0.30 ml at STP. When mixtures were used, 0.30 ml of each gas was present in the mixture in the loop. The feed rate of helium was 10 ml/min for all runs with the sampling valve; the reaction temperature was 180°C.

For the adsorption studies via step functions, the feed rate was 90 ml/min, corresponding to a residence time of about 18 sec in the mixed reactor. For all experiments the inlet concentrations of gases were CO, 5 mole%; O_2, 2.5 mole%; and CO_2, 5 mole%. The temperature was 160°C and the pressure was atmospheric. The results to be presented show that CO is not adsorbed, CO_2 is reversibly adsorbed, and O_2 is irreversibly adsorbed, i.e., not removed by switching back to helium. Thus the initial state of the catalyst must be defined as to oxygen content. A normal catalyst is one which has been exposed to a mixture of 2.5% O_2 in helium and then exposed to pure helium for 6 min. A partially reduced catalyst is a normal catalyst treated with 5% CO for 6 min followed by helium. If the catalyst is exposed to CO for about 90 min, evolution of CO_2 finally ceases; we call the result a reduced catalyst.

RESULTS

The results are given for the interactions of the various gases and gas mixtures with the catalysts in various states. After this information has been presented we shall
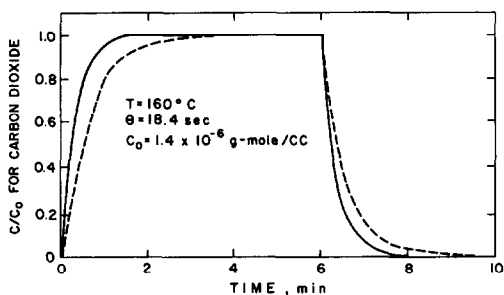
FIG. 1. Oxygen adsorption on partially reduced supported catalyst.

FIG. 2. Carbon monoxide adsorption on normal supported catalyst.

deduce the probable sequence of steps for CO oxidation.

Oxygen

Oxygen adsorbs on a partially reduced catalyst as shown in Fig. 1. The solid line is what would occur if there were no adsorption, just mixing in the gradientless reactor. The dashed line is the actual curve, showing considerable adsorption; the desorption portion of the curve shows that the adsorption is irreversible. After this treatment, a second switching to the oxygen mixture showed no further adsorption. No CO_2 (or O_2) was produced in either case.

A mixture of 0.30 ml O_2 and 0.30 ml O_2** showed no exchange of any kind; in particular, no O_2* (MW 34) was observed. All these characteristics of the oxygen–NiO interaction are in accord with those given in the review by Nováková (6). Kuchynka and Klier (7) used electrical conductivity measurements to show that at 150°C the irreversibly adsorbed oxygen is present as O^-; the same result is obtained by Bielanski and Najbar (8) by a titration method. We shall refer to this adsorbed oxygen as $O\alpha$, where the α site is probably a nickel atom.

Carbon Monoxide

When CO is passed over a normal (supported) catalyst, its behavior is shown in Figs. 2 and 3. The CO reacts with adsorbed oxygen to produce CO_2. If the par-
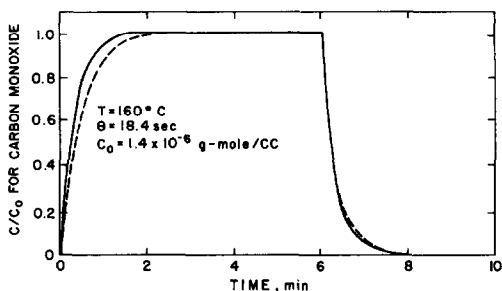
tially reduced catalyst produced is now reexposed to oxygen, the curve of Fig. 1 is obtained; no CO_2 is produced. Thus, no CO adsorbs as such; the apparent adsorption of Fig. 2 is actually reaction. If the CO treatment is continued beyond 6 min until no more CO_2 is produced, we then find that no CO is adsorbed on this reduced catalyst. The CO_2 produced is 12.2×10^{-5} gmole/g of NiO or 2.1×10^{14} molecules/cm^2 of NiO. When this catalyst is now reoxidized to the normal state, 6.0×10^{-5} gmole/g of NiO of oxygen is adsorbed, agreeing approximately with simple stoichiometry.

Pulse studies using CO* and C*O were also performed. It is however difficult to analyze the various isotopic forms of the CO effluent because recombination reactions in the mass spectrometer tend to cloud the analysis. A rhenium filament was used; no exchange of CO_2 species was observed. There seems little doubt that the CO is unable to exchange with the catalyst
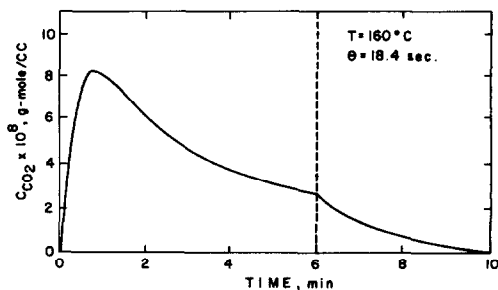

FIG. 3. Carbon dioxide production on normal supported catalyst.

surface. One should note, however, that there is a possibility of exchange with CO_2 adsorbed on the surface in some form and this will be discussed later. This interaction implies some exchange in the presence of CO_2 that would be formed if the CO were being oxidized during a pass over the catalyst. The results of the monitoring of the $m/e = 28, 29, 30, 31$ peaks suggest that the exchange is via CO_2 as an intermediate or adsorbed on the catalyst and not by direct CO–CO or CO–catalyst exchange. It was found that the $31/29$ ratio increased for a sample of C^*O (MW 29) over pure NiO as well as over the supported catalyst as the surface oxygen became progressively exchanged during successive runs during which O^* had been added to the surface. Data noted in the $CO–O_2$ interaction description below further this view.

Carbon Dioxide

Figure 4 shows that carbon dioxide is reversibly adsorbed on the supported catalyst. Integration based on the areas between the dashed and solid lines indicates that the quantities adsorbed and desorbed are the same and equal to 9.0×10^{-5} gmole/g of NiO or 1.5×10^{14} molecules/cm^2 of NiO. The same results are obtained on a partially reduced and on a reduced catalyst, so that it seems probable that CO_2 adsorbs on a site separate from the removable O_2 and that the presence of $O\alpha$ has no effect on CO_2 adsorp-
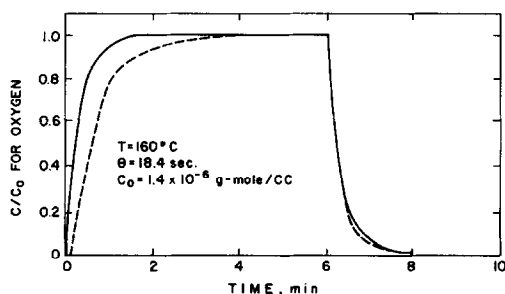
tion. We shall call the site for CO_2 adsorption $O\beta$, where the O is strongly held, probably O^{2-}. The CO_2 is then associated with the oxygen in $O\beta$.

Whereas the CO and O_2 do not exchange with any of the catalyst surfaces, the oxygen of CO_2, on the other hand, readily exchanges on the support as well as on the supported NiO and pure NiO. The silica surprisingly is a very active exchange catalyst even after a 500°C treatment in dried helium performed to discern whether residual H_2O was the medium of exchange. A purer silica (Davison grade 62) was tried and it also showed rapid CO_2 oxygen exchange. Whereas the silica was able to exchange the oxygen of CO_2, there was no evidence of adsorption of CO_2 on the surface. For pure NiO exchange involving the carbon took place to some extent. This implies a residual carbon and more probably carbon–oxygen species on the surface. Such a bound carbon-containing surface species may or may not be directly involved in the oxidation reaction. The isotopic content of such a species is exchangeable by interaction with CO_2 and does not exchange with oxygen or directly with carbon monoxide; however if there is oxygen present on the catalyst the interaction and exchange with CO will take place via the CO_2 formed from the CO in the oxidation process.
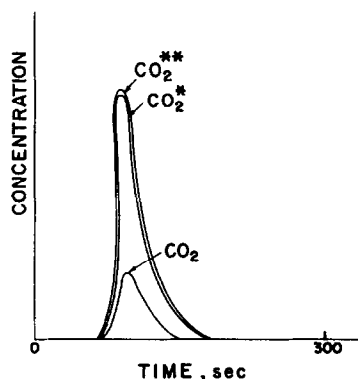
Figure 5 shows the CO_2^{**} exchange

FIG. 4. Carbon dioxide adsorption on normal supported catalyst.

FIG. 5. CO_2^{**} exchange at 180°C on a normal unsupported catalyst containing no O^*.

over pure NiO catalyst. As already mentioned C*O₂ exchange also takes place, so we postulate that there is another site on the catalyst such as $CO_3\gamma$. CO_2 cannot be desorbed from these sites by helium at 180°C, but C* and O** are exchangeable on the sites. The exchange is rapid.

As a result of the ability of the silica support to exchange the oxygen on carbon dioxide, most of the following results will be discussed with respect to the pure nickel oxide as the interpretation is clearer for the unsupported NiO.

Carbon Monoxide and Oxygen

Figure 6 shows the response of a normal catalyst containing some oxygen-18 to a pulse of C*O (0.3 ml) and to a pulse of C*O and O₂** (0.3 ml of each). The carbon monoxide-29 reacts with surface oxygen to form mostly C*O₂, reflecting the composition of the adsorbed oxygen on the catalyst. If to this pulse is added O₂**, the oxidation is somewhat enhanced, but the proportion of O* in the carbon dioxide
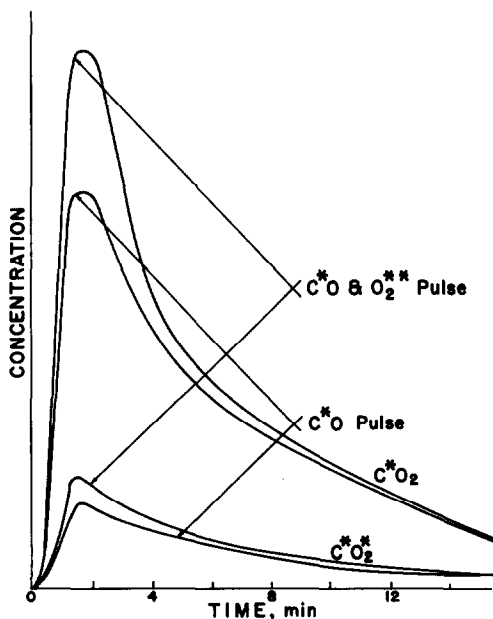
formed is not appreciably changed. The added O₂** in the pulse has been mixed with the large pool of ¹⁶O on the surface and has merely kept the level of Oα up while the C*O is reacting.

From Figs. 2 and 3 we can see that the rate of CO oxidation is influenced by some kind of adsorbed species formed from CO(g) and Oα. When the carbon monoxide is shut off (Fig. 3) the rate of CO_2 production abruptly decreases, so CO_2 desorption or decomposition of an intermediate is probably not rate limiting. Also, Fig. 2 shows that the first output of the CO conversion is rapidly finished; probably $CO_2\alpha$ is rapidly desorbed, but the residual reduction of the surface in the presence of CO goes through a more complicated path.

The experiment of Fig. 6 was repeated on a partially reduced catalyst. As expected, the pulse with O₂** now gave a higher proportion of C*O₂*, although the absolute heights were smaller.

The isotopic products of the reaction between CO and oxygen on the supported catalyst were clouded by the rapid exchange between the CO_2 formed and the support as well as the NiO surface. For this reason the unsupported catalyst was also used for following the isotopic distribution obtained by oxidizing CO*. The
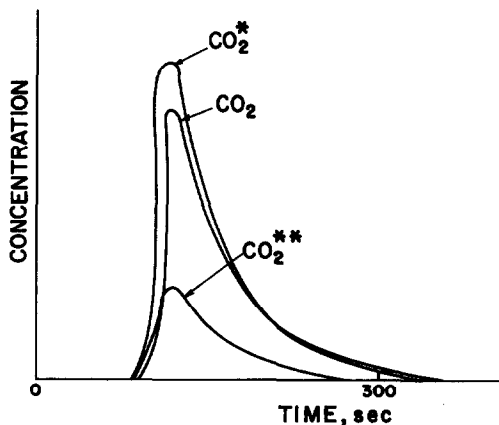

FIG. 6. C*O oxidation on normal supported catalyst at 180°C containing some O*.

FIG. 7. CO* oxidation at 180°C on normal unsupported catalyst containing no O*.

result is shown in Fig. 7 (the times are shorter than those of Fig. 6 because the reactor is smaller). The surprising result is that considerable CO_2** is formed; as a matter of fact, since any CO_2** formed would exchange to form CO_2* and CO_2 (Fig. 5), the inherent production of CO_2** is higher than that shown. The presence of this product indicates that a surface intermediate is formed from two molecules of CO*; a CO_3 species would contain no more than one O* and produce at most CO_2* and no CO_2**.

Carbon Dioxide–Oxygen

Gas-phase oxygen did not seem to influence the isotopic content of exchanging carbon dioxide, as is seen in Fig. 8. The presence of O_2** has no effect on the amount or extent of exchange of C*O_2 over the supported catalyst. No noticeable effect was seen on the reduced catalyst in the same experiment. This result is consistent with that of Fig. 8; the CO_2 exchanges with the carbon–oxygen species already on the catalyst, and the presence of O_2** in the gas has essentially no effect.
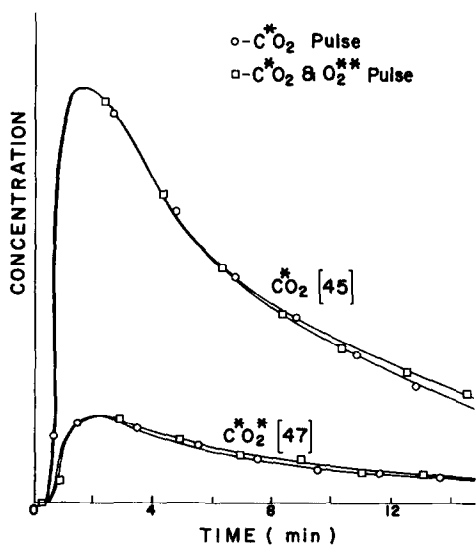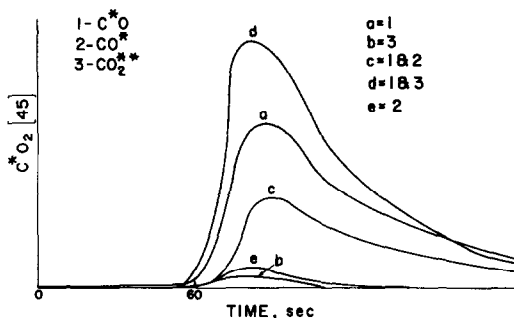
FIG. 9. CO–CO_2 interactions at 180°C on normal unsupported catalyst; C*O_2 response.

Carbon Dioxide–Carbon Monoxide

A mixture of C*O plus CO_2** was used to determine the interaction between carbon monoxide, which does not reversibly adsorb to any noticeable extent, and CO_2 reversibly adsorbed on the surface. Figures 9–12 represent the mass spectral response for the predominant isotopic products of this interaction over pure NiO. Both the C*O_2 and C*O_2* products are enhanced by the addition of carbon dioxide (CO_2-48) to a C*O pulse; furthermore C*O_2* is proportionately more enhanced than in the C*O_2 peak by the addition of CO_2** to the reactant (Figs. 9 and 10, curves a and d). Keeping in mind that any CO_2 formed will exchange with other sites on the surface, it seems obvious that this promotion of the CO oxidation by a reversible CO_2** involves abstraction of a
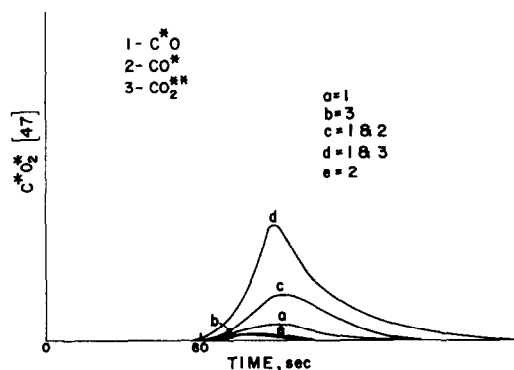
FIG. 8. C*O_2 adsorption on normal supported catalyst at 180°C containing some O*.

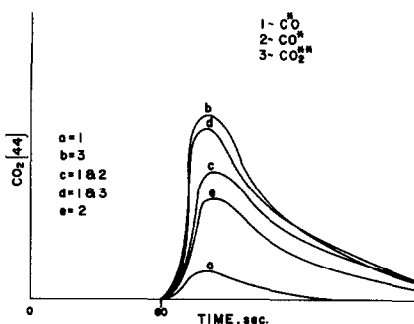FIG. 10. CO–CO_2 interactions at 180°C on normal unsupported catalyst; C*O_2* response.

Fig. 11. CO–CO$_2$ interactions at 180°C on normal unsupported catalyst; CO$_2$ response.

labeled oxygen from the adsorbed CO$_2$ complex and not any surface oxygen that may be a part of this complex. This is further supported by the noted change in the C*O$_2$ to C*O$_2$* ratio from that which is found for curve a in Figs. 9 and 10, which reflects the simple isotopic CO oxidation ratio wh ch will reflect the oxygen content of essentially all the O-containing surface species. There is little change in the isotopic oxygen content of the exchanged CO$_2$** on the addition of C*O (Figs. 11 and 12, curves b and d). That the interaction with carbon monoxide does not affect the exchange to any great extent implies that there may be different sites for the exchange and the carbon monoxide–carbon dioxide interaction. It has already been mentioned that CO$_2$** exchanges with an irreversibly adsorbed carbon–oxygen species whether or not adsorbed oxygen (Oα) is present. Since the presence of C*O does not seem to affect the CO$_2$**
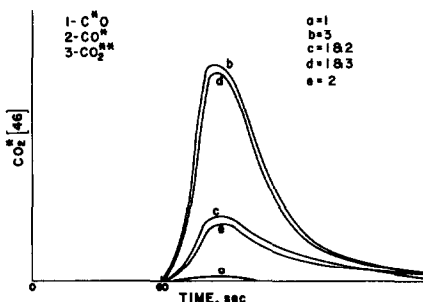

Fig. 12. CO–CO$_2$ interactions at 180°C on normal unsupported catalyst; CO$_2$* response.

exchange, this view is supported: the CO$_2$ exchanges on what we might call a CO$_3\gamma$ site, independent of the presence of CO or O$_2$. However, CO does not exchange with the surface unless CO$_2$ (reversibly adsorbed) is present. Combining this fact with the result shown in Fig. 7 strengthens the argument that CO oxidation passes through a two-carbon complex, probably formed by CO$_2$Oβ and CO(g).

There is also an increase in the C*O$_2$* formation during the oxidation of C*O by addition of CO* and a simultaneous decrease in the formation of C*O$_2$ (Figs. 9 and 10, curves c and a). Since a 50–50 mixture of C*O on CO* would mean that any carbon dioxide–carbon monoxide interaction on the surface would have an equal probability of involving a carbon dioxide formed from C*O or from CO*, the presence of CO* would be expected to decrease the C*O$_2$ and increase the C*O$_2$* via this enhancement. This reasoning also requires that the coverage of the intermediate be limited. Similarly the CO$_2$ peak increases for the mixture of C*O–CO* compared to pure CO*; however the overall expected effect of increasing the CO$_2$ while decreasing the CO$_2$* is clouded by the carbon dioxide exchange involving the labeled carbon as well as oxygen and the increased carbon dioxide produced from the mixture.

DISCUSSION

A summary of the exchange results at 180°C is shown in Tables 2 and 3. Table 2 represents the interactions found for two-component pulses where the gases may reversibly adsorb on the surface of the catalyst and interact either between species on the catalyst or between the adsorbed species and the gas molecules. It can be noticed that the only exchange that takes place is between CO and CO$_2$ and between CO$_2$ and the surface with the possibility of CO$_2$–CO$_2$ exchange.

It is, however, difficult to differentiate

TABLE 2

INTERACTION BETWEEN GASES REVERSIBLY
ADSORBED ON SURFACE AND IN
GAS PHASE

CO_2	CO	O_2	both present in gas phase
Exchange of O (and C)	Exchange of O	No exchange	CO_2
	None (except via CO_2)	Reaction no exchange	CO
		No exchange	O_2

between CO_2–CO_2 exchange and CO_2 surface exchange because of the extensive CO_2 exchange with the surface, as is seen in Table 3. CO–CO_2 exchange on the other hand takes place rapidly with the oxidation of the CO and possible reduction of the CO_2; however, our difficulty of analysis of the CO peaks did not allow differentiation between $C*O$ + CO_3S → $C*O_2$ + CO_2S and $C*O$ + CO_2 → $C*O_2$ + CO. As the O_2 had little effect on the CO peaks, we were able to exclude CO exchange with oxygen. CO–CO exchange occurs only via the CO_2 formed from oxidation, and since that which is formed is already on the surface it enhances the CO exchange more greatly than does CO_2 alone.

TABLE 3

INTERACTION BETWEEN GASES AND SPECIES
IRREVERSIBLY ADSORBED ON SURFACE

CO_2	CO	O_2	in gas phase
Exchange of C and O	No exchange[a]	No exchange	on surface CO_2
None adsorbed	None adsorbed	None adsorbed	CO
Small effect if at all	Reaction	No exchange	O_2

[a] See text.

The interaction between the gases and the surface as single components is shown in Table 3. CO_2 exchanges via an interaction with a residue of carbon–oxygen species with a partial equilibration of the carbons in the intermediate such that both carbon and oxygen may exchange. There may be a small effect of CO_2–O_2 exchange on the surface but it is greatly clouded by the CO_2 surface exchange. The CO does not adsorb as CO but as an oxygenated species; it only reacts with adsorbed oxygen and does not exchange with any surface species. Oxygen is adsorbed irreversibly and does not show any exchange with the surface oxygen or CO_2.

The exchange of CO_2 and the oxidation of CO* are shown in Figs. 5 and 7. The oxygen-18 content ($\chi_{18} = 2(48) + 46/(48 + 46 + 44)$) of the carbon dioxide produced from CO_2^{**} + OS exchange changed from a measured value of 0.943 in the pulse of Fig. 5 to a value of 0.613 after exchange. From this we can estimate the original isotopic mole fraction of the carbon dioxide product of the oxidation of Fig. 7. If we assume that the surface of the catalyst contains predominantly ^{16}O at all times, we can assume that each exchange interaction involves the replacement of the exchanged oxygen with oxygen-16 only. On this basis the values of the various CO_2 species actually found as in Fig. 7 must have been, before exchange, approximately 20% CO_2^{**}, 50% CO_2^*, and 30% CO_2.

An oxidation of CO* dominated by CO + Oα → CO_2 would yield 100% CO_2^* prior to exchange. A mechanism involving CO + O_2S → CO_3S → CO_2 + OS as the predominant pathway would yield a product ratio of 67% CO_2^* and 33% CO_2 as the primary products prior to exchange. Our results on pure NiO, however, indicate an intermediate involving two carbons so that there is the possibility of CO_2^{**} formation via an intermediate such as $C_2O_2^{**}O_2$. If this intermediate con-

tained equivalent oxygen the product percentage based on statistics would be CO_2, 16.7%; CO_2*, 66.6%; CO_2**, 16.7% for the oxygen content of the surface oxygen species being 100% O_2 and that of the gas phase being 100% CO*.

Several factors would tend to increase the percentages of CO_2** and to a greater extent CO_2 relative to the percentage of CO_2* as was found from our data. The most probable explanation is that CO_2 is adsorbed on an oxygen firmly attached to the surface; we have already called this reversibly adsorbed species $CO_2O\beta$. Recall that CO_2** is supposed to exchange with the C and O in the $CO_3\gamma$ sites. Then some CO* probably reacts with CO_2*$O\beta$ already formed from CO* to form the intermediate C_2O_3**$O\beta$, where the fourth oxygen does not exchange. This intermediate is probably removed by oxidation with an $O\alpha$ to form $2CO_2$, with 25% CO_2**, 50% CO_2*, and 25% CO_2 produced.

Probable Sequence of Steps

Excluding exchange, which we will assume occurs on sites separate from those involved in oxidation because of lack of effect of oxygen either in the gas phase or on the surface on the extent of exchange, we find two main interactions on the NiO sample at 180°C. The first involves oxidation of carbon monoxide by irreversibly adsorbed oxygen and the second involves a pathway for oxidation of CO by reversibly adsorbed CO_2. The following sequence is suggested.

1. $O_2 + 2\alpha \rightarrow 2\,O\alpha$
2. $CO + O\alpha \rightarrow CO_2\alpha$
3. $CO_2\alpha + O\beta \rightleftarrows CO_2\,O\beta + \alpha$
4. $CO_2\,O\beta \rightleftarrows CO_2 + O\beta$
5. $CO_2\,O\beta + CO \rightleftarrows C_2O_3O\beta$
6. $C_2O_3O\beta + O\alpha \rightarrow$
   $\qquad 2\,CO_2 + O\beta + \alpha.$

At 180°C the predominant surface species would be $O\alpha$ and $CO_2O\beta$. In separate steady-state rate measurements (21)

we show that CO_2 inhibits the reaction at 150°C, but the effect is reduced at higher temperatures; there is less inhibition at 180°C. This observation is accounted for by supposing that the equilibrium in step 3 is pushed toward $CO_2O\beta$ at higher temperature, so that little $CO_2\alpha$ is present. Some $CO_2(g)$ may be produced by step 4, but the isotope studies at 180°C indicate that much of the CO_2 is formed via steps 5 and 6. The two-carbon intermediate is present in low concentrations so that on the $O\beta$ sites, $CO_2O\beta$ is the most abundant species.

We are now doing transient studies of adsorption and reaction in order to find numerical values for the parameters which describe the sequence of steps given above.

CONCLUDING REMARKS

The oxidation of CO over NiO has been the subject of many studies. Although oxide catalysts seem to be more sensitive to the method of preparation than metal catalysts, we find quite good agreement between our results and those of others, who have made their NiO from $Ni(NO_3)_2$, $Ni(OH)_2$, or $NiCO_3$, and pretreated at temperatures from 200°C to as high as 1000°C. We do not give references to all other work but rather mention recent studies which seem particularly relevant.

Many studies have been done at about 25°C, where CO is adsorbed on NiO (3,9,10). However, Gravelle *et al.* (11) noted that CO adsorption decreases with temperature, and Gandhi and Shelef (12) found negligible adsorption above 140°C. We have confirmed these results. Exchange studies of CO and CO_2 have been done mostly at 25°C and rarely at 100°C (13,14). Klier and co-workers have studied this also, mostly at 25°C, e.g., Klier and Jiratova (15).

As already mentioned, Winter (16,17) and Kuchynka and Klier (7) found irre-

versible adsorption of O_2 as O^- at 150°C and below 200°C, in accord with our results. However, Gorgoraki and Kasatkima (*18*) found homonuclear oxygen exchange from 25 to 250°C on NiO.

The only mention of a two-carbon intermediate known to us is by Keulks and Chang (*19*). They suggest that on silver CO_2 adsorbs on top of O ads and that two CO_2–O ads units form the intermediate $C_2O_4·20$ ads. In our results we would identify a CO_2 combined with a $CO_2O\gamma$ site for exchange, and a CO combined with CO_2–$O\beta$ as $C_2O_3O\beta$ as a step in the oxidation of CO.

In our previous work on N_2O decomposition, we found that N_2 was not adsorbed and that temperature above 300°C was needed to make the decomposition go by driving off the oxygen. It would be interesting to study CO oxidation in this higher temperature range to see how the CO would react with the now reversibly adsorbed oxygen.

We mention finally the work of Kobayashi and Kobayashi (*20,21*) who used the transient method to study CO oxidation on MnO_2 at −15°C and N_2O decomposition at 348°C. In both cases they deduced mechanisms similar to those we propose. However, their reaction rates were very slow; their transients lasted up to an hour, whereas ours were over in a few hundred seconds at most.

ACKNOWLEDGMENTS

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