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CO Interaction with the Surface of Thermally Activated CaO and MgO

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Adsorption of $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$ on CaO and MgO, pretreated at 1000 K, has been studied at 40–300 K. A number of surface CO compounds have been detected, which differ in their thermal stability or sensitivity with respect to oxygen. From the measured isotopic shifts and frequencies the force constants of some compounds were calculated. The first product arising after CO admission is the "carbonite" CO_2^{2-} ion, which is the result of CO interaction with a coordinatively unsaturated oxygen ion. At temperatures higher than 100 K the carbonite ion reacts with excess CO to produce the dioxoketene $O{=}C{=}CO_2^{2-}$ ion. Further reactions with CO give rise to more complex compounds, both oxidized and reduced. In the presence of oxygen, carbonite ions and reduced CO compounds are readily oxidized into carbonates; at low temperature, some intermediate products of oxidation were registered. Reversible interaction of CO with the surface O^{2-} ions is responsible for the catalytic reaction of low-temperature homomolecular isotopic exchange of CO on the surface of basic oxides. It is supposed that the established mechanism of CO activation by oxygen ions is typical for other reactions on the surface of basic and alkali-promoted catalysts.

INTRODUCTION

The surface metal ions of CaO and MgO exhibit very low electron-accepting ability and cannot form strong coordinative bonds with adsorbed molecules, as has been shown earlier in experiments with ammonia, pyridine, and benzonitrile as test molecules (*1*, *2*). Proton-donating properties of the surface hydroxyl groups of these oxides, estimated from the OH frequency shifts on adsorption of basic molecules, also turn out to be extremely poor (*3*). In the same way, the results of low-temperature CO adsorption (*4*) on samples pretreated under mild conditions show the absence of strong adsorption sites on the surfaces of alkali-earth oxides. However, evacuation at high temperatures causes dramatic changes in the adsorption properties. CO adsorption on samples thermally activated in this way gives rise to rather complicated surface species, which have strong absorption in the UV and visible spectral region (*5*). Zecchina and co-workers (*6*, *7*) studied the IR spectra of such systems at 300 K and came to the conclusion that at the surface of thermally activated CaO and MgO at room temperature CO disproportionation occurs, which leads to the formation of negatively charged polymeric structures like $(CO)_n^{2-}$ and carbonate ions. However, because of the great number of structures arising and due to the complexity of the spectra observed the proposed assignments as well as the suggested mechanism of the surface reactions accounting for the formation of certain species cannot be considered finally established.

Preliminary results (*4*) have demonstrated that the IR spectra of CO adsorbed on CaO or MgO at liquid nitrogen temperature differ significantly from those observed at 300 K. This means that by following the changes in the spectra of adsorbed CO during heating from low temperatures to 300 K

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we can hope to gain new information on the mechanism of CO transformations on the surface of alkali-earth oxides. Moreover, the half-width of the bands registered at 77 K is usually comparatively low and more detailed data on the composition and structure of surface species can be obtained from the frequency shifts caused by isotopic substitution.

Thus the purpose of this work is the thorough examination of CO adsorption at 40–300 K on calcium and magnesium oxides. The influence of the sample pretreatment conditions, adsorption temperature, heating in the presence of the adsorbate, evacuation, and treatment in oxygen or other gases on the spectrum of adsorbed CO has been investigated. To establish the structure of the species arising, experiments on the adsorption of isotopically substituted $^{13}C^{16}O$ and $^{12}C^{18}O$ molecules, as well as the adsorption on the ^{18}O-enriched CaO surface, were performed, and the observed isotopic shifts were compared with those calculated for the hypothetical structures of different geometry and force constants.

EXPERIMENTAL

The stainless-steel IR cell for liquid nitrogen temperature studies used in the present work is shown in Fig. 1. By means of this cell spectra of surface species could be registered at 77–300 K either in the presence of gaseous phase or after evacuation. In those cases when adsorption was studied at temperatures below 77 K, or when the exact temperature of adsorption was a subject of a special interest, the previously described cell for liquid helium temperature (*8*) was employed. To eliminate the radiation thermal exchange of the warm walls with the cooled central part of the cell, the latter was surrounded by a polished copper screen. For better thermal contact of the sample with the cooled environment, before taking the spectra, 0.5–2 Torr (1 Torr = 133.3 $N \cdot m^{-2}$) of gaseous helium was usually admitted into the inner volume of the cells. Special experiments with a thermocouple, pressed directly into the sample, have shown that with gaseous helium even for highly absorbing samples the pellet temperature is not more than 5° higher than that of the cooled walls. However, on evacuation or when the sample was heated, despite all precautions, the accuracy of temperature measurement was less, typically about ±10 K. Not knowing the real sample temperature in every case, we write here "77 K," meaning that the cell was cooled with liquid nitrogen.

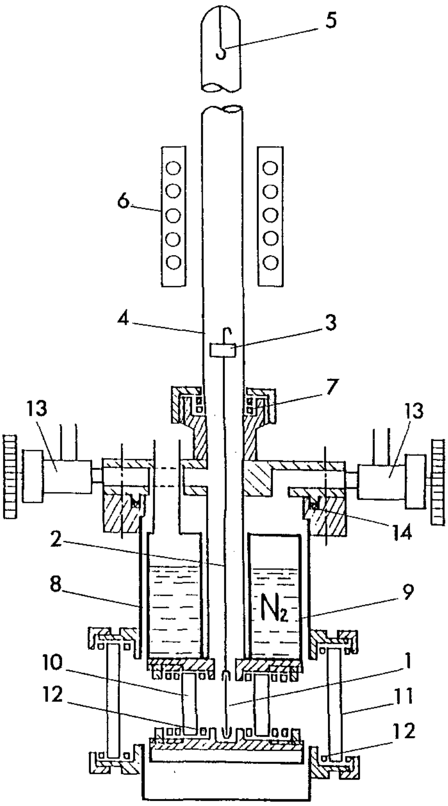


FIG. 1. Stainless-steel IR cell for studying the spectra of adsorbed molecules at 77 K. (1) sample, (2) sample holder, (3) anchor of magnetic stainless steel, (4) quartz tube, (5) hook for fixing the holder in the upper position, (6) furnace, (7) Viton O-ring, (8) cell body, (9) cooled part of the cell, (10) BaF_2 windows, (11) NaCl windows, (12) indium gaskets, (13) valve, (14) Teflon gasket.

To combine the spectroscopic and adsorption measurements, both the cells were equipped with deformation PMGD-1 pressure gauges. Knowing the gas pressure in a special dosing volume before adsorption, we obtained the surface coverage. For reversible forms of adsorption, band intensity measurements at different pressures and temperatures enabled us to find the isosteric heat of adsorption from the plot of log P against $1/T$.

Spectra were registered on a Specord 75 IR or on a UR-20 (Carl Zeiss, Jena) infrared spectrometer with a typical slit width of 1–3 cm^{-1} and an accuracy of band position and isotopic shift determination for narrow bands not worse than ±1 cm^{-1}. When registering spectra of CaO in the 800- to 700-cm^{-1} region, BaF_2 plates were inserted in the reference beam to compensate for the absorption of the cell windows and the sample background.

Thermoactivated samples of oxides were prepared from pellets, preliminarily pressed from commercial $Ca(OH)_2$, $MgCO_3$, or $Mg(OH)_2$ powders by heating them under vacuum at 1000–1100 K for 0.5–1 h. The initial thickness of the pellets varied from 20 to 60 mg cm^{-2}. The BET surface area was about 40 and 100 m^2/g for CaO and excarbonate MgO samples, respectively. When the dependence of the sample properties on the pretreatment temperature was studied, samples were brought into contact with water vapour at 300 K and then evacuated at the desired temperature. To prepare the ^{18}O-enriched samples, CaO was saturated with $H_2{}^{18}O$ with subsequent thermal decomposition *in vacuo*. To achieve a higher ^{18}O content the procedure was repeated 2–3 times.

Commercial CO with natural isotopic composition and ^{13}CO containing 84.7% of this species were used. $^{12}C^{18}O$ with an enrichment of about 70% was prepared by passing $^{12}C^{18}O_2$ over heated charcoal at 1200 K. Before admission into the cell, gases were purified by passing through a trap cooled with liquid nitrogen. If necessary, traces of oxygen from commercial CO were removed by contact with a metal sodium mirror.

Calculations of the vibrational spectra were carried out by use of the molecular approach, i.e., the weak bonds between the surface compound and the surrounding atoms of adsorbent were neglected. Control estimations have shown that these interactions only slightly affect the frequencies in the 2000- to 800-cm^{-1} region and have practically no influence on the isotopic shifts. For postulating the bond lengths, the known correlations between force constants and lengths of the bonds were used. The values of valence angles were varied between wide limits.

The force constants were determined from the condition of best coincidence of the isotipic shifts in the calculated frequencies with the observed shifts in the absorption bands, while the deviation of the calculated frequencies from those obtained from the experiment should not exceed a certain limit. The advantage of this method against the ordinarily used method of fundamental frequency reproduction is a lower uncertainty in the obtained solutions as a consequence of the narrower error limits for the isotopic shift reproduction (1–2 cm^{-1}) compared with those of the fundamental frequencies (10–20 cm^{-1}).

RESULTS

CO Adsorption on CaO

CO interaction with the surface of thermally activated CaO has been studied in a wide range of temperatures from 40 to 300 K. As can be seen from Fig. 2, the spectra obtained after adsorption at 60, 130, and 300 K are quite different, and those registered at low temperatures contain narrow bands suitable for isotope shift measurements. As a rule, raising the temperature produces irreversible changes in the spectrum and new bands arising on heating the sample remain after subsequent cooling. Effects caused by temperature lowering, on the contrary, are completely reversible, and bands of new species arising at intermediate or room temperatures, such as

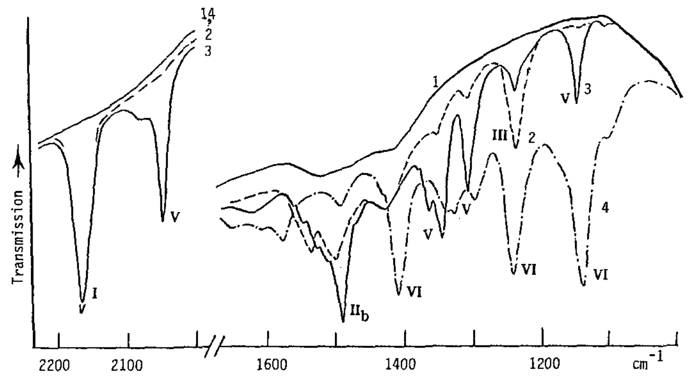


FIG. 2. IR spectrum of CaO after treating *in vacuo* at 1000 K and cooling by liquid nitrogen (1), adsorption of CO: 1.5 molec · nm^{-2} at 60 K (2), 5 Torr at 130 K (3), and 5 Torr at 300 K (4).

those which appear after CO adsorption at 130 K (curve 3), can be stabilised by cooling the sample with liquid nitrogen.

Bands of adsorbed CO reveal different sensitivities with respect to various kinds of sample treatment. Figure 3 illustrates the influence of thermoevacuation and admitting oxygen on the spectrum of CO adsorbed at 300 K. Some bands disappear immediately after oxygen addition with the concurrent growth of new bands of oxidized species, while others remain intact in the presence of oxygen, but disappear after heating under vacuum.

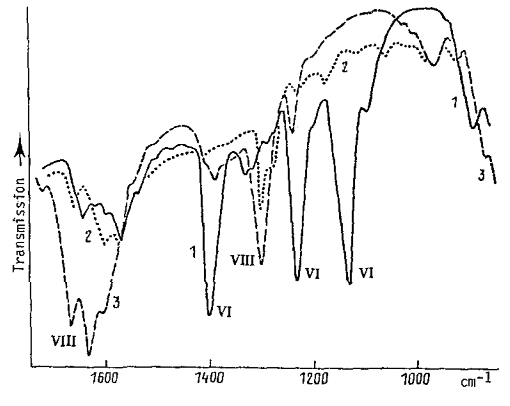


FIG. 3. Influence of thermoevacuation and oxygen admissoin on the spectrum of CO adsorbed on CaO. (1) CO (5 Torr), adsorbed at 300 K on CaO thermoactivated at 1000 K. (2) After evacuation for 20 min at 470 K. (3) Spectrum 1 after addition of oxygen.

It was possible to distinguish at least nine groups of several bands which appear and vanish simultaneously and whose relative intensities remain unchanged after all kinds of sample treatments. In Figs. 2 and 3, and in the text below, these groups of bands are labled with different Roman numbers. We believe that the bands of one group are due to the same surface species; however, the idea of simultaneous formation of two different substances as a result of one surface reaction followed by their coherent destruction cannot be ruled out completely.

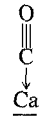
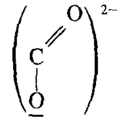
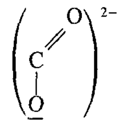
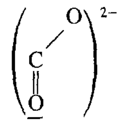
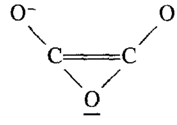
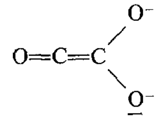
Data on band positions and their isotopic shifts observed after $^{13}C^{16}O$ and $^{12}C^{18}O$ adsorption, as well as after adsorption on ^{18}O-enriched CaO samples, are presented in Table 1 for six main groups of bands. Isotopic shifts were measured not only for the highest but also for medium isotope content when for the structures containing several substitutable atoms their exchange in different positions results in the appearance of several unequally shifted bands. In such cases all the observed shifts with respect to the initial band are given in Table 1. If the isotopic splitting of the bands could not be resolved, the shift values observed for the highest isotope content are presented.

Adsorption at Low Temperatures

A triplet of highly superimposed bands in the region of the free CO molecule absorp-

TABLE 1

Positions and Isotopic Shifts of IR Bands Arising after CO Adsorption on CaO

Compound	ν (cm^{-1})	Δν (cm^{-1})				Proposed structure
	$^{12}C^{16}O$ on $Ca^{16}O$	$^{13}C^{16}O$ on $Ca^{16}O$	$^{12}C^{18}O$ on $Ca^{16}O$	$^{12}C^{16}O$ on $Ca^{18}O$	$^{12}C^{18}O$ on $Ca^{18}O$	
I	2163	48	52	0	—	
	2155	48	52	0	—	
	2145	48	52	0	—	
IIa	1485	32	32[a]	0	—	
	890	20	10[a]	—	—	
	743	3	11	22	—	
IIb	1480	32	32	0	—	
	850	17	0	9	—	
	717	8	4	—	—	
III	1227	32	5	16	—	
	865	15	8	—	—	
	733	5	—	—	—	
IV	1195	10; 29	12; 22	0	—	
	982	12; 22	0	7	7	
V	2038	4; 50; 56	26	0	—	
	1356	—	—	—	—	
	1339	15; 35	0	3	—	
	1300	10; 28; 37	10	2	—	
	1137	5; 20; 23	8	13	—	
	760	—	4	4	—	
VI	1403	38	9	0	9	$(CO)_n^{2-}$
	1234	28	16	0	4; 19	
	1135	10; 27	0	0	6	

[a] After several cycles of adsorption–desorption.

tion, which arise in the spectrum of thermoactivated CaO samples after CO adsorption at 40–150 K, represents the first group of bands. The three components are not actually due to one surface structure, but to three kinds of adsorbed molecules only slightly differing from each other. The first to arise at the coverage of about 0.1 molec nm^{-2} are the side bands of the triplet at 2163 and 2145 cm^{-1}, while as the coverage grows the central band at 2155 cm^{-1} becomes more intense. The bands attributed to group I can be removed by prolonged evacuation at 80 K or by heating the sample. Addition of oxygen does not affect their intensity. Shifts in the group I bands on carbon or oxygen isotopic substitution are practically the same as those for the free CO molecule, and these bands do not move after surface oxygen substitution.

The second compound, whose spectrum is presented in Fig. 4, can be of at least two

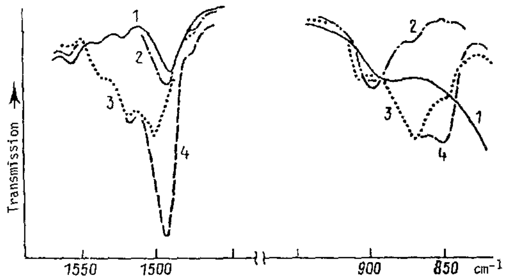


FIG. 4. IR spectrum of CaO, pretreated at 1000 K, after adsorption of CO (0.2 molec nm^{-2}) at 300 K (1), cooling by liquid nitrogen (2), and subsequent additional adsorption of 3 (3) and 9 (4) molec nm^{-2} of CO at 77 K.

different kinds. One of them, denoted in Table 1 as IIa, absorbs at 1485, 890, and 743 cm^{-1} and arises after adsorption of the first doses of CO (up to 0.2 molec nm^{-2}) at 77–300 K on thermoactivated CaO (curves 1 and 2). The bands of this compound disappear after evacuation for 0.5 h at 300 K or immediately on admitting oxygen at 77–300 K.

After adsorption of ^{12}CO and ^{13}CO mixture at 300 K the 1485-cm^{-1} band is split into two distinct peaks, one coinciding with the initial band and the other shifted downward by 32 cm^{-1}. The same value of the isotopic shift was observed after ^{12}C^{18}O adsorption; however, in contrast with the case of ^{13}CO, the intensity ratio of the split band components does not at first reflect the proportion between C^{16}O and C^{18}O molecules in the adsorbed mixture, the band due to the unsubstituted compounds being more intense. Nevertheless, after several cycles of adsorption and evacuation some redistribution of intensity occurs which indicates the elimination of this discrepancy between the isotopic content of gaseous and adsorbed species.

The isotopic shifts of the low-frequency bands of the IIa compound at 890 and 743 cm^{-1}, because of their higher half-width, were measured only for the maximum concentrations of the heavy isotope.

If the sample with CO adsorbed at room temperature is cooled to 77 K, the bands of compound IIa become more pronounced and practically do not change their position. However, when CO is adsorbed after cooling the sample and the bands of compound II appear together with those of compound I, the former bands appear instead at 1495, 865, and 733 cm^{-1}. The same shifted bands can be observed after addition of CO at 77 K to the sample with CO preadsorbed at room temperature in the form of the compound IIa. Removal of the excess adsorbate by pumping at 77 K, resulting in the disappearance of the group I bands, restores the initial spectrum of the IIa compound.

The bands of another kind of compound II at 1480, 850, and 717 cm^{-1} can be observed only at 40–130 K (curve 4 in Fig. 4) after adsorption of rather high amounts of CO. The intensity of these bands reaches its maximum at overall coverages of about 9 molec nm^{-2}. At 77 K this form of adsorption, denoted in Table 1 as IIb, exists only in equilibrium with the gas phase and disappears after short evacuation. The estimated isosteric heat of adsorption for the IIb compound was found to be about 30 kJ mol^{-1}.

Heating to 300 K in the presence of gaseous CO results in the disappearace of both the IIa and the IIb groups of bands; however, only the IIb structure can be restored by subsequently lowering the temperature, along with compound I. The group II bands also disappear after addition of oxygen with simultaneous formation of bands due to oxidized compounds.

Adsorption of ^{13}C^{16}O and ^{12}C^{16}O mixtures causes the splitting of both the 1480- and the 850-cm^{-1} bands of the IIb structure into two components. After using a mixture of ^{12}C^{18}O with ^{12}C^{16}O the 1480-cm^{-1} band is also divided into two maxima; however, that at 850 cm^{-1} remains unshifted. On the other hand, after ^{12}C^{16}O adsorption onto the ^{18}O-enriched samples, the band at 850 cm^{-1} is split into bands at 850 and 840 cm^{-1}, while the 1480-cm^{-1} band does not display any detectable shift.

A strong band attributed to compound III appears at 1227 cm^{-1} after adsorption of the first doses of CO at temperatures as low as 40 K, together with the bands of compound I and II (Fig. 2). Raising the temperature to 130 K results in the destruction of this compound accompanied by simultaneous formation of species IV and V. Two other bands assignable to the same compound were detected at 865 and 733 cm^{-1}. Compound III is also very sensitive to oxygen and disappears immediately after admitting O_2 into the cell.

Adsorption of the $^{13}C^{16}O$ and $^{12}C^{16}O$ mixture gives rise to two maxima corresponding to the 1227-cm^{-1} band with a shift of 32 cm^{-1}, while in the case of $^{12}C^{18}O$ only a distortion of the contour with a shift of the maximum by 5 cm^{-1} could be observed. However, adsorption of $^{12}C^{16}O$ on the ^{18}O-enriched surface results in the appearance of a new component of this band shifted down by 16 cm^{-1}, and for $^{12}C^{18}O$ the shift is as high as 22 cm^{-1}.

After CO adsorption on CaO at 77 K, in addition to the bands due to the I–III compounds, absorption in the 1550- to 1520-cm^{-1} region, which is not sensitive to the addition of oxygen, but which diminishes on heating the sample, arises.

Adsorption at Intermediate and Room Temperatures

The bands of the other CO compounds appear at temperatures higher than 77 K. CO adsorption at 130–150 K results in the absorption bands attributed to the I, II, IV, and V compounds. Two narrow bands of compound IV arise at 1195 and 982 cm^{-1} after admitting CO at 130 K. Slight heating of the sample, evacuation, or addition of oxygen removes these bands. After adsorption of the $^{13}C^{16}O$ and $^{12}C^{16}O$ mixture each of the bands due to compound IV splits into three components; admission of $^{12}C^{18}O$-containing mixture also causes splitting of the 1195-cm^{-1} band into three constituents, while the 982-cm^{-1} band remains untouched.

The most numerous group of bands arising as a result of a surface reaction of CO on CaO is presented in Table 1 under Roman number V. These bands appear at 130–150 K together with those of compound IV, but unilke the latter do not vanish after evacuation or admission of oxygen at low temperature, but gradually diminish on heating the sample to 300 K.

On CaO there exist perhaps two kinds of compound V. Originally after CO addition the band at 2033 cm^{-1} appears among the other bands of group V, which after removal of the excess adsorbate (mainly compound I), is shifted to 2038 cm^{-1}. The positions and isotopic shifts for this very low-temperature form in the spectra recorded at 77 K are presented in Table 1. As the temperature is increased some redistribution of intensities occurs in the spectrum of compound V, resulting in weakening of the 2038- and 1356-cm^{-1} bands and growing of the bands of another modification of compound V at 2072 and 1324 cm^{-1}. The other bands of the compound in question are, evidently, common for both the modifications. The overall integrated intensity of the compound V bands drops on heating the sample (simultaneously with the growth of the bands due to the high-temperature compounds VI) and in the spectrum registered at 300 K is rather low.

Changes in the position of the high-frequency band at 2038 cm^{-1} after adsorption of mixtures of different isotopic content are illustrated in Fig. 5. The position of this band is characteristic for an isolated carbonyl group. Application of ^{13}C-containing mixtures results in a splitting of the band into two main components with a shift of about 50 cm^{-1}; however, at low $^{12}C^{16}O$ concentrations the initial band turns out to be shifted downward by 4 cm^{-1}. In the spectra registered with better resolution for the mixtures of $^{13}C^{16}O$ close to equimolar one can see that each of the two components really consists of two poorly resolved peaks about 4 cm^{-1} apart. ^{18}O substitution in the adsorbed molecules produces splitting of the 2038-cm^{-1} band into two components

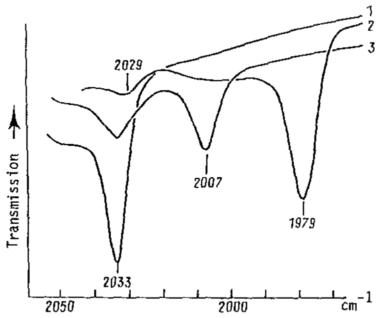


FIG. 5. The high-frequency band of compound V, observed for different isotopic compositions of the adsorbed gas. (1) $^{12}C^{16}O$, (2) $^{13}C^{16}O$, and (3) $^{12}C^{18}O$, adsorbed at 130 K on thermoactivated CaO.

with the distance about half that of the analogous splitting of the compound I bands.

The low-frequency bands of compound V also reveal complex splitting on ^{13}C substitution, giving three or four components. Introduction of ^{18}O gives rise to not more than two constituents, the splitting distance being different for oxygen substitution in the molecule and in the surface of the adsorbent.

At room temperature and high surface coverages only the bands of groups VI and VIII–IX can be seen. The bands of compound VI appear after CO adsorption at 300 K or on heating the sample with CO preadsorbed at low temperature (77 K) simultaneously with the growth of the bands of compounds VIII–IX and diminution of those due to species V. Subsequent cooling of the sample to 77 K in the absence of gaseous CO does not affect the position of the bands, but additional CO adsorption in form I shifts the 1403- and 1135-cm^{-1} bands to higher wavenumbers, up to 1416 and 1155 cm^{-1}. The bands of compound VI disappear after evacuation at temperatures not lower than 470 K or after oxygen treatment at 300 K (see Fig. 3), in accordance with the earlier results of Coluccia and co-workers (*7*). If the sample has been brought into contact with oxygen at 77 K after CO adsorption, subsequent heating does not lead to the formation of compound VI. The lemon-yellow colour of the CaO samples observed after CO adsorption (*5*) arises and disappears together with the bands of compound VI.

Oxidation of Adsorbed CO

When oxygen is admitted to the CaO sample with preadsorbed CO, strong absorption, which we attribute to the oxidized compounds VII–IX, arises in the 1700- to 1500-, 1400- to 1200-, and 1050- to 950-cm^{-1} regions. The reaction leading to these species takes place at 300 K as well as at 77 K and is accompanied by vanishing of the bands due to compounds II, III, and IV. A certain part of the oxidized compounds appears, perhaps, in the absence of oxygen, since the absorption at 1650–1550 and 1350–1250 cm^{-1} arises alongside compound VI bands when the sample is heated after CO adsorption at low temperatures.

It should be noted that the spectra of the oxidized compounds are not quite the same when they are obtained in different ways. Thus, for instance, in the latter case above when they are formed without oxygen admission, absorption in the 1050- to 950-cm^{-1} region was not registered. It seems that the broad bands consist of a set of components, each corresponding to a certain structure in a definite environment.

To obtain, if possible, one of these structures we performed experiments by oxidizing compound IIa at 77 K, when no other forms of adsorbed CO were on the surface. For this purpose, after adsorption of a small amount of CO at 300 K on thermally activated CaO, the cell was cooled by liquid nitrogen, gaseous helium was inserted for stabilising sample temperature, and only then was a portion of oxygen allowed into the volume with CaO. The observed changes in the spectrum caused by oxidation and subsequent heating of the sample are shown in Fig. 6.

As expected, low-temperature oxidation leads to a set of new well-defined bands, whose position and isotopic shifts could be measured with satisfactory accuracy. Fig-

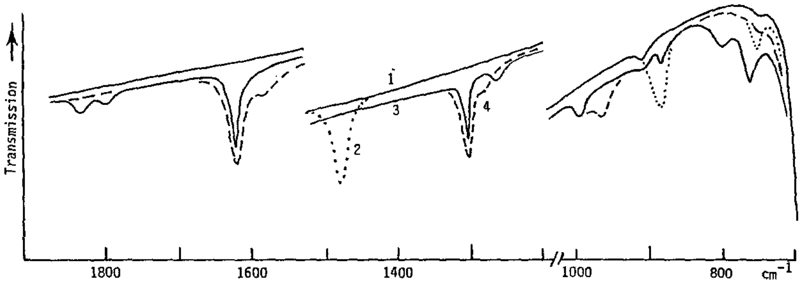


FIG. 6. IR spectrum of CaO after pretreating at 1100 K (1), adsorption of $^{12}C^{16}O$ (0.2 molec nm^{-2}) at 300 K and cooling to 77 K (2), adding oxygen at 77 K (3), and raising the temperature to 300 K (4).

ure 7 illustrates the influence of isotopic substitution in the adsorbed CO on some of the bands, and all the measured frequencies and isotopic shifts for oxidized compounds are presented in Table 2. Different behaviour of the bands with respect to heating the sample provides the means to separate the bands arising on oxidation of compound IIa into three groups, denoted in Table 2 as VII, VIIIa, and VIIIb.

The group VII bands arise immediately after oxygen addition at 77 K and disappear after heating the sample to 300 K. This compound has unexpectedly high-frequency bands in the 1840- to 1770-cm^{-1} region. Compound VIIIa appears together with VII, but does not change when the temperature is raised. Bands attributed to compound VIIIb appear and grow when the sample is heated, simultaneously with the disappearance of those of group VII. The band positions, isotopic shifts, and thermal stability of compounds VIIIa and VIIIb are very close to each other.

After CO adsorption at 77 K compounds II and III arise together. In this case, along with the group VII and VIII bands, a new set of bands appears after admission of oxygen at 77 K, denoted in Table 2 as group IX. These bands grow when the temperature is raised and belong, apparently, to the product of compound III oxidation.

The bands of oxidized compounds VIII–IX do not disappear after CaO treatment *in vacuum* at 470 K when all the other compounds are decomposed. The complete disappearance of all the bands of adsorbed CO may be achieved at temperatures not lower than 900 K. If CO is adsorbed on CaO at 77 or 300 K in a mixture with O_2, or if the CO used has an impurity of oxygen, compounds II–VI do not arise at all, and the

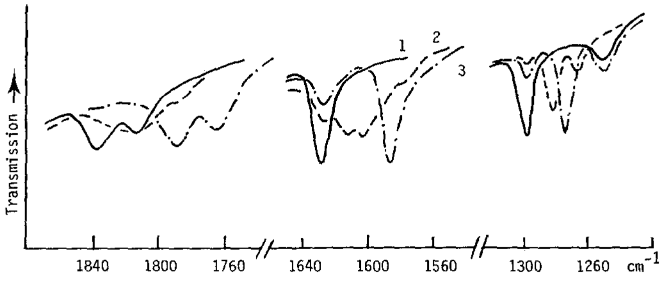


FIG. 7. IR spectrum of CaO after admitting $^{16}O_2$ at 77 K to the sample with small quantities (about 0.2 molec nm^{-2}) of $^{12}C^{16}O$ (1), $^{12}C^{18}O$ (2), or $^{13}C^{16}O$ (3), preadsorbed at 300 K.

TABLE 2

Positions and Isotopic Shifts of IR Bands Due to the Products of Oxidation of CO_2^{2-} Ions on CaO

Compound	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})		
	$^{16}O_2$ on $^{12}C^{16}O_2^{2-}$	$^{16}O_2$ on $^{13}C^{16}O_2^{2-}$	$^{16}O_2$ on $^{12}C^{18}O_2^{2-}$	$^{18}O_2$ on $^{12}C^{16}O_2^{2-}$
VII	1838, 1813	48	30	0
	1777	55	—	32
	1257	5	25, 50	0
	798	14	18	6
	781	22	—	—
	750	0	—	0
VIIIa	1630	45	13, 26	0
	1299	27	16, 30	0
	988	5	10	0
	876	29	4	0
VIIIb	1586	46	13	6
	1278	21	—	0
	965	3	10	0
	856	27	4	0
IX	1665	0	14	20
	1554	0	—	14
	1394	34	4	4
	1346	41	6	11
	1308	32	24	0
	1249	27	10	10
	762	5	7	7

only visible result of adsorption is the formation of compounds VIII–IX, as well as compound I, if the temperature is low enough.

CO Adsorption on MgO

CO interaction with the surface of thermally activated magnesium and calcium oxides produces spectra which have much in common. In accordance with our earlier data (*4*) low temperature CO adsorption on MgO pretreated with water vapour and evacuated at temperatures below 650 K results in the appearance of one absorption band at 2150 cm^{-1}. As the pretreatment temperature is raised a more detailed picture in this region could be observed. In agreement with recent work by Escalona Platero and co-workers (*9*), after adsorption of the first doses of CO a band at 2165 cm^{-1} appears, which moves with growing coverage toward lower wavenumbers. Another band arises at 2146–2140 cm^{-1}. The position and isotopic shifts of these bands are analogous to the group I bands of CaO. After both $^{13}C^{16}O$ and $^{12}C^{18}O$ adsorption (Fig. 9), the shift of these bands is about 50 cm^{-1}.

If the pretreatment temperature is higher than 700 K, new bands, whose intensities reach a maximum for samples evacuated at 1000–1100 K, appear in the spectrum of adsorbed CO. As can be seen from Fig. 8, the spectrum of CO adsorbed on thermoactivated MgO at low temperature also differs from that observed after the sample has been heated to 300 K, while the latter is almost identical with the spectrum which was described earlier for CO adsorbed at room temperature (*6*).

The band at 1472 cm^{-1}, which also arises after CO adsorption at 77 K, displays a certain resemblance to the 1480-cm^{-1} band of

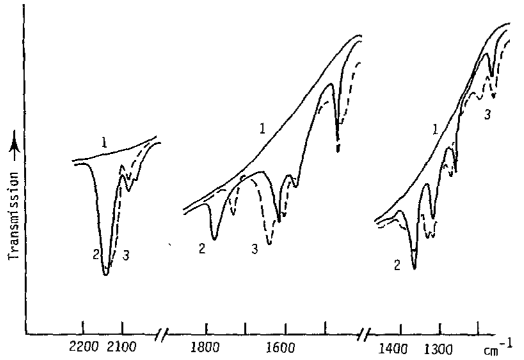


FIG. 8. IR spectrum of MgO after pretreatment at 1000 K (1), adsorption of CO (5 Torr) at 130 K (2), and raising the temperature to 300 K and repeated cooling in the presence of CO to 77 K (3).

compound IIb on CaO. It disappears after oxygen treatment or evacuation at 77 K and when the sample is heated to 300 K, but is restored after the sample is repeatedly cooled in the presence of CO. However, while the ^{13}C substitution splits this band into two maxima 37 cm^{-1} apart, admission of a mixture of $^{12}C^{18}O$ and $^{12}C^{16}O$ produces splitting into three peaks at 1471, 1459, and 1445 cm^{-1} (Fig. 9), in contrast with the structure of the IIb band of CaO, which on ^{18}O substitution gives rise to no more than two components. Moreover, we did not succeed in the search for the other, low-frequency bands of this compound on MgO.

Bands at 1670 and 1570 cm^{-1} in the MgO spectrum are, apparently, analogous to the absorption in the 1550- to 1520-cm^{-1} range of CO adsorbed on CaO, since they were observed under similar conditions.

In the spectrum of CO adsorbed on MgO there is a group of bands which corresponds to those of compound V on CaO. Intensity variations on heating the sample enable us to distinguish three kinds of these species with bands at 2099, 1378; 2084, 1367; and 2109, 1355 cm^{-1}. The bands at 1320 and 1166 cm^{-1} are, evidently, common to all kinds of this structure. Unlike those of compound V on CaO, these bands do not disappear after the sample is heated to 300 K, although they significantly diminish and can be completely removed by evacuation at 450 K. Oxygen admission at low temperatures does not affect their intensity. The isotopic shifts in the bands of this group are very close to those observed after adsorption of ^{13}C and ^{18}O-containing mixtures on CaO.

At room temperature along with these bands a group of comparatively weak maxima is present at 1455, 1278, and 1200 cm^{-1}, and more intense bands at 1740, 1655, 1325, and 1015 cm^{-1}. After the oxygen treatment at 300 K the 1455-, 1278-, and 1200-cm^{-1} bands disappear, just like the group VI bands of CaO, while the remaining four bands become enhanced, in a manner similar to those of the oxidized compound VIII on CaO.

In addition to the above-mentioned features, in the spectrum of CO adsorbed at low temperatures on MgO a number of bands arise which have no apparent analogs in the CaO spectrum. Thus there are bands produced at 1785 and 1260 cm^{-1} which are absent in the spectrum recorded at 300 K. Evacuation at 100 K for 0.5 h eliminates their intensity, while the addition of oxygen does not influence them. After adsorption of $^{13}C^{16}O$ and $^{12}C^{16}O$ mixtures each of these bands becomes split into two maxima with shift values of 45 and 17 cm^{-1}, respectively.

In order to discover the nature of the ac-

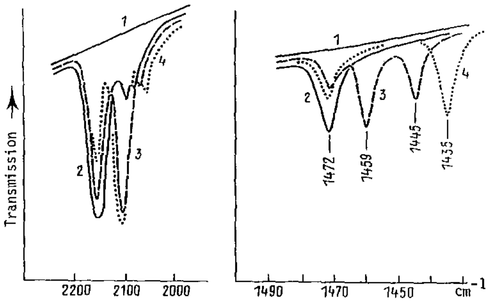


FIG. 9. IR spectrum of MgO after evacuation at 1000 K (1) and adsorption of $^{12}C^{16}O$ (2), $^{12}C^{18}O$ (3), or $^{13}C^{16}O$ (4) at 5 Torr and 77 K.

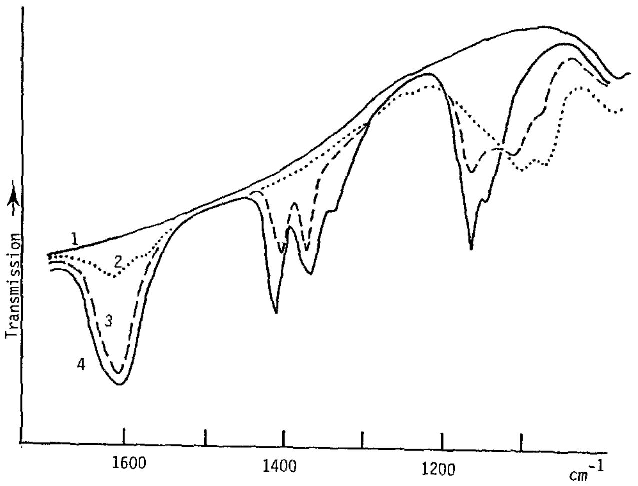


FIG. 10. IR spectrum of MgO after evacuation at 1000 K (1), adsorption of NH_3 at 300 K, removing the excess of gas and cooling to 77 K (2), subsequent addition of 5 Torr CO (3), and heating the sample to 300 K (4).

tive sites on these basic oxides it seemed attractive to use poisoning of some sites by other molecules. It was shown earlier (*10*) that on the surface of thermoactivated MgO adsorbed ammonia partly dissociates to form surface OH and NH_2 groups. Our attempt to adsorb CO on a MgO sample with preadsorbed ammonia after pumping off the excess NH_3 at 300 K showed that all the CO compounds described above, with the exception of the compound I, do not arise on such a surface, but a new group of bands appears at 3470, 3440, 2820, 1610, 1410, 1360, 1170, and 1150 cm^{-1} (Fig. 10). The bands are enhanced after heating to 300 K and may be removed by pumping at elevated temperatures.

DISCUSSION

Molecular Adsorption (Compound I)

The isotopic shifts of the group I bands on ^{13}C and ^{18}O substitution, like the frequencies themselves, are close to those of a free CO molecule in the gas phase. Taking into account also that these bands can be removed by evacuation at 77 K, we assign them to CO molecules weakly bound to the surface. The bands in the 2150- to 2140-cm^{-1} range may be attributed to the vibrations of unspecifically adsorbed molecules, and those which are shifted to higher wavenumbers compared with the free molecule can be assigned to molecules which form a weak coordinative bond to the surface metal ions. For MgO the frequency of such molecules (2165 cm^{-1}) is somewhat higher than that for CaO (2163 cm^{-1}). In both cases, however, it is much lower than values characteristic of CO adsorption on strong Lewis sites. These results support the concept of the weak electron-accepting power of Ca^{2+} and Mg^{2+}, which is a little higher for surface magnesium ions. The shift of the band toward lower frequencies on coverage growth for MgO or increase of the 2157-cm^{-1} band in the case of CaO could be the result of lateral interaction between the adsorbed molecules (*9, 11*).

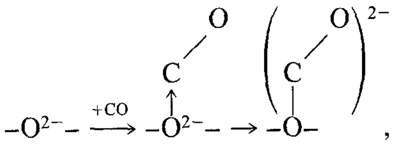
Compound II: Dioxocarbene (Carbonite) CO_2^{2-} Formation

Taking into account the proximity of the band positions and isotopic shift values of the IIa and IIb compounds, we suppose them to have a similar structure. Inasmuch as after adsorption of both ^{13}C- and ^{18}O-labeled molecules each band is split into two maxima, the compound in question should contain one C and one O atom from the adsorbed molecule. In addition, the shift of the 890- to 850-cm^{-1} band for the ^{18}O-enriched samples points to the fact that surface oxygen is also incorporated in the structure of this compound. The character of the isotopic splitting of the bands due to compound II enables us to state that it consists of one C and two nonequivalent oxygen atoms, one of the latter originating from the molecule, and the other from the surface of the adsorbent. There is no evidence for the existence of two carbon atoms in this compound, as was supposed in Ref. (*7*), where the bands arising at 1485 and 890 cm^{-1} after adsorption of CO on CaO at 300 K were assigned to the dimers $(CO)_2^{2-}$, containing no surface oxygen.

The presence of three bands in the spectrum of compound II is in accordance with the proposed three-atom structure which should have three normal modes. Calculation of the normal vibrations for the $O{-}C{-}\underline{O}$ and $\underline{M}{-}O{-}C{-}O{-}\underline{M}$ models, where $\underline{M}$ is a surface metal atom, confirmed the possibility of assignment of the bands at about 1480, 890–850, and 740–720 cm^{-1} to the OCO group, the high frequency band corresponding to the stretching mode of the stronger C–O bond, and the other two to the coupled stretching and bending vibrations of the weak $C{-}\underline{O}$ bond and the $O{-}C{-}\underline{O}$ angle. (Note: $\underline{O}$ signifies an oxygen atom of the oxide adsorbent).

From the observed frequencies and isotopic shift values the force constants of compound IIa were calculated to be 8.8 and 3.2 mdyn Å^{-1} for $k(C{-}O)$ and $k(C{-}\underline{O})$, respectively, and 2.0 mdyn Å rad^{-2} for $k(O{-}C{-}\underline{O})$, while the valence angle could vary in the range 90–150°, and the force constant of bond interaction $h(O{-}C{-}\underline{O})$ was 0.3–0.7 mdyn Å^{-1}. Such low frequencies and force constant values for compound II, compared with those of free CO and CO_2 molecules, can be explained only by a high negative charge of the CO_2 group, identifying compound II with the CO_2^{2-} ion which arises as a result of the CO molecule attaching itself to a coordinatively unsaturated surface O^{2-} ion (*12–14*). This assignment is borne out by the spectra of $M_2^{2+}CO_2^{2-}$ compounds stabilised in argon or nitrogen low-temperature matrices (*15*, *16*). Stretching C–O frequencies of such complexes which have two nonequivalent C–O bonds fall in the regions of 1450–1330 and 1190–980 cm^{-1}, and force constants of C–O bonds for the compound K_2CO_2 were found to be 7.5 and 4.2 mdyn Å^{-1} while $h(O{-}C{-}O)$ was 0.65 mdyn Å^{-1}, all the values being close enough to those found for the IIa compound. To compare with this, the $k(C{-}O)$ values for the single-charged CO_2^- anion are about 12 and 9.1 mdyn Å^{-1} (*15*, *16*) and for the neutral CO_2 molecule even 15.5 mdyn Å^{-1}.

The formation of the CO_2^{2-} ion may be illustrated by the scheme



, where the CO molecule participates in the role of a Lewis acid, just as in the cases of CO_2 or SO_3 adsorption with the formation of surface carbonate or sulphate ions. By analogy with nitrites, sulphites, phosphites, and other anions with the valence of the central atom two units lower than its highest value, the CO_2^{2-} compound can be referred to as a "carbonite" anion (*13*). The possible reaction of surface basic oxygen ions with CO molecules leading to the formation of CO_2^{2-} ions was proposed also by Lamotte and co-workers to explain the IR spectra of CO adsorbed on thoria (*17*).

The 1472-cm^{-1} band which arises in the low-temperature spectrum of CO adsorbed on MgO, in its position and behaviour, is very much like one of the bands of compound IIb in the spectrum of CaO (1480 cm^{-1}). The results of isotopic substitution, presented in Fig. 9, point to the same composition, despite the fact that the other bands of this compound on MgO were not registered. In fact, splitting of this band into two maxima on ^{13}C substitution reveals the presence of one C atom participating in this vibration. Appearance of three bands with almost equal shifts between them and the intensity of the central maximum approximately twice as high as that of the side bands after adsorption of the equimolar mixture of $C^{16}O$ and $C^{18}O$ corresponds to the case when two oxygen atoms occupy equivalent or almost equivalent positions. Normal vibration analysis reveals that only the band of the antisymmetrical stretching mode of O–C–O with a valence angle between 120 and 130° can have such isotopic shifts. From the observed frequency value the combination of the force constants k(O–O) − h(O–C–O) can only be calculated and turns out to be about 6.8 mdyn $Å^{-1}$. For the most probable values of the interaction force constant h in the 0.5- to 2-mdyn $Å^{-1}$ region the constant k should be about 7–9 mdyn $Å^{-1}$, which is typical for CO_2^{2-} ions. Thus, the 1472-cm^{-1} band can also be assigned to the same CO_2^{2-} structure, but, in contrast with those arising on CaO, with equivalent C–O bonds.

Reactivity of CO_2^{2-} Ions and Isotopic Exchange

The CO_2^{2-} ion can be regarded as a product of removing two protons from the formic acid molecule. It could therefore be expected that the ion has a high proton affinity and after capture of a proton will turn into the formate ion CHO_2^-. To check this supposition we have studied the influence of the addition of small amounts of water vapour on the spectrum of compound IIa on CaO. The results are presented in Fig. 11. Admission of water results in the disappearance of the IIa bands at 1485 and 890 cm^{-1} and in the appearance of new bands at 2820, 1605, and 1370 cm^{-1}, which in accordance with Ref. (*1*) should be attributed to formate ions. The latter bands do not arise if the bands due to compound II are absent from the initial spectrum, even in the presence of other forms of adsorbed CO, e.g., compound VI. They also do not appear after CO adsorption on the hydrated sample. This means that formate ions do not arise as a result of CO interaction with surface OH groups, at least at 300 K.

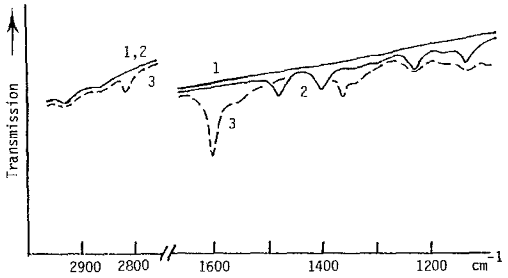


FIG. 11. IR spectrum of CaO after pretreatment at 1000 K (1), adsorption of CO (about 0.2 molec nm^{-2}) (2), and addition of water vapour (3).

The high sensitivity of the CO_2^{2-} species to oxygen treatment implies that the ions can readily be oxidized with formation of carbonate-like species. Subsequent removal of oxygen and repeated CO adsorption at 77 K do not lead to the formation of CO_2^{2-} ions; however, the ability of the sample to form the low-temperature (IIb) carbonite structure can be restored by heating the sample to 300 K followed by cooling to 77 K. This result enables us to consider the CO_2^{2-} ions as intermediates in the reaction of catalytic CO oxidation and the coordinatively unsaturated oxygen ions responsible for the formation of the group II compounds as active sites for this reaction.

The presence of two equivalent oxygen atoms in the CO_2^{2-} structure is possible when the formation of the bond between the carbon atom and surface oxygen ion is accompanied by attachment of the oxygen atom of the CO molecule to one or several surface metal ions in such a way that the coordinations of both the oxygen atoms become equal. If the adsorption in carbonite-like form is reversible, then in the case of equivalent oxygen atoms the CO molecule can desorb containing the oxygen atom which initially belonged to the surface. This implies the possibility of isotopic exchange with the surface oxygen. For MgO, where the carbonite ions with the band at 1472 cm^{-1} contain two equivalent oxygen atoms, appearance of the band at 1445 cm^{-1} due to the compound $^{12}C^{18}O_2^{2-}$ with two substituted oxygen atoms after $C^{18}O$ adsorption may be considered as evidence for such exchange. The presented data therefore enable us to explain the mechanism of low-temperature homomolecular isotopic exchange of CO, which is known to occur on MgO (*18*).

The possibility of the isotopic exchange reaction on the CaO surface, where the asymmetrical carbonite ions occur with two *unequivalent* C–O bonds, is evidently limited by the process of intramolecular transformation: $^{16}\underline{O}{-}C{=}^{18}O \rightarrow {}^{16}O{=}C{-}^{18}\underline{O}$. The isotopic exchange at 77 K with surface oxygen on CaO does not take place, since both the oxygen atoms in the II structures can be substituted separately for the ^{18}O isotope. At room temperature, however, spectral data testify for the existence of such an exchange.

In fact, after allowing small amounts of $C^{18}O$ into contact with CaO at 300 K, initially only the bands due to unsubstituted $C^{16}O_2^{2-}$ ions arise, identical with those produced by adsorption of normal $C^{16}O$. It is not until after several cycles of adsorption and evacuation that the isotopic content of ^{18}O in the carbonite ions, estimated from the intensity ratio of components in the split 1485-cm^{-1} band, approaches the value for the gaseous mixture. Meanwhile, the low-frequency 890-cm^{-1} band, corresponding to the vibration of C against the surface oxygen atoms, proves also to be shifted by 10 cm^{-1}. At low temperatures the analogous shift can only be observed after CO adsorption on the surface preliminarily enriched with the ^{18}O isotope. Thus, the carbonite CO_2^{2-} ion with unequivalent oxygen atoms can also be the intermediate in the CO isotope exchange reaction, but not at low temperatures.

The fact that there is isotopic exchange of CO with surface oxygen was confirmed by mass-spectrometric analysis of gaseous CO over CaO sample (*19*). Measurement of the ^{18}O content in the adsorbate before adsorption and after reaching equilibrium with the surface oxygen at 300 K for known quantities of gas and adsorbent provides a means for estimating the surface concentration of the oxygen ions which are capable of exchange under these conditions. Thus, the obtained value of about 0.3 site nm^{-2} is close to the concentration of sites responsible for the formation of structure IIa (about 0.2 site nm^{-2}). We should therefore exclude the possible supposition that the exchange occurs on some other sites prior to carbonite formation, and this supports the conclusion that these are the CO_2^{2-} ions which account for the exchange and are the intermediates in this reaction.

Compound III

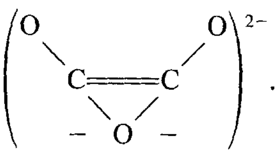
According to the isotopic substitution data for the 1227-cm^{-1} band, compound III must also have in its composition one carbon and two oxygen atoms, one of the latter originating from the sample surface. The mean wavenumber values of the two highest frequency bands of this compound falls in the region 1300–1000 cm^{-1}, which is characteristic of the stretching vibrations of CF_2 or O_3 molecules or the NO_2^- ion which is isoelectronic with CO_2^{2-} (*17*). That is why we attribute this band to one more kind of carbonite ion.

Calculations for such three-atom structures have shown that the observed frequency shifts of the 1227-cm^{-1} band may be obtained for the antisymmetrical stretching vibration of a $O{-}C{=}\underline{O}$ group with a valence angle of 120–150° and two nonequivalent bonds, whose force constants differ by about 1.5 mdyn Å^{-1}, the more strong bond being that with the surface oxygen atom $\underline{O}$. The symmetric vibration frequency falls in the 1000- to 750-cm^{-1} region, a considerable part of which is obscured by the intense bands of the compounds II. The lack of reliable spectral data on the isotopic shifts of low-frequency vibrations does not permit us to obtain unequivocally the force constants of the bonds, which turn out to depend on the unknown interaction bond constant $h(\mathrm{O{-}C{-}O})$. For the most probable h values from the 0- to 1-mdyn Å^{-1} region, $k(\mathrm{C{-}O})$ and $k(\mathrm{C{-}\underline{O}})$ should be 3.5–5 and 5–6.3 mdyn Å^{-1}, respectively.

Compound IV

There are only two bands in the CaO spectrum, at 1195 and 982 cm^{-1}, which could be attributed to compound IV. However, after both oxygen and carbon atom substitution the high-frequency band splits into three almost equally separated components, thus implying that at least two carbon and two oxygen atoms participate in the corresponding vibration of this compound. These atoms apparently occupy equivalent or almost equivalent positions, since otherwise not three but four components should be observed.

In the low-frequency vibration (the 982-cm^{-1} band) mainly carbon atoms take part, because after $C^{18}O$ adsorption the 982-cm^{-1} band remains unshifted. After substitution of surface oxygen, however, this band displays a detectable shift, pointing to the presence of a surface oxygen atom in the structure of this compound. A possible structure accounting for the band observed is a CO dimer bound to a surface oxygen atom:

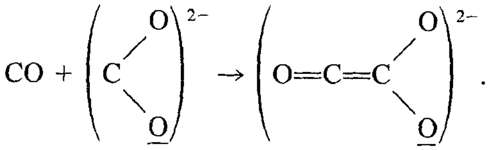


Bands of other fundamental vibrations for this structure are evidently less intense and are obscured by strong bands of compound V and bulk absorption. On MgO such a form of adsorption was not found.

Compound V: Dioxoketene $C_2O_3^{2-}$ ion

Compound V, judging from the great number of its absorption bands, has a rather complicated structure. The position of the most high-frequency band is characteristic for the uncoupled C–O bond in carbonyl-like compounds. Nevertheless, either on ^{13}C or ^{18}O substitution the change in the reduced mass of the CO group is practically the same and for frequencies near 2000 cm^{-1} corresponds to a shift of about 50 cm^{-1}, while the shift in the 2038-cm^{-1} band after $C^{18}O$ adsorption is twice as low. This fact can be regarded as an indication of a collective vibration of several adjacent bonds. In fact, after adsorption of ^{12}CO and ^{13}CO mixture the bands due to compounds of intermediate isotopic composition were detected, which although slightly (4–6 cm^{-1}) shifted against the bands of the initial or completely substituted compounds are distinctly observable. It is natural to conclude that the compound in question contains two nonequivalent carbon atoms and that, as was supposed by Guglielminotti *et al.* (*6*) for the analogous band in the MgO spectrum, the 2038-cm^{-1} band is due to the antisymmetrical stretching vibration of the ketene group O═C═C.

Splitting of the 1300- and 1137-cm^{-1} bands into four components after adsorption of ^{13}CO-containing mixtures supports the conclusion about the presence of two carbon atoms in compound V, while the significant shifts after $^{12}C^{18}O$ adsorption (the 1300-cm^{-1} and 1137-cm^{-1} bands) and after $^{12}C^{16}O$ interaction with the ^{18}O-enriched surface (1137-cm^{-1} band) enable us to affirm that the ketene group is bound to one surface oxygen and one oxygen atom from a CO molecule. The species answering such enquiry should have the "dioxoketene" structure $(OCCO_2)^{2-}$ and can be the result of the interaction of a CO molecule with the surface carbonite ion:



This process is analogous to the above reaction of CO_2^{2-} ion formation, the difference being in the source of the unshared pair of electrons. Here it is not the surface coordinatively unsaturated oxygen atom, but the divalent carbon of the carbonite ion previously formed on the surface. Similar reaction with CO leading to the formation of ketene $O{=}C{=}CH_2$ is well known for carbene CH_2 (*21*) and such a reaction for the surface CO_2^{2-} ions once again shows that they can be considered dioxocarbene, the compound of divalent carbon isoelectronic with CF_2.

The $(O{=}C{=}CO_2)^{2-}$ species should have four stretching vibrations in the region above 700 cm^{-1}. The 2038-cm^{-1} band is due to the asymmetric vibration ν_{as} of the ketene group. Its frequency and shift values can be adequately reproduced from are following force constants: k(C–O) = 14–15, k(C–C) = 7–8.5, h(O–C–C) = 1.7–2 mdyn Å^{-1}. The three other vibrations are the symmetrical mode of the ketene group and two stretching vibrations of the CO_2^{2-} fragment. If the force constants of the C–O bonds have an order of magnitude of about 5 mdyn Å^{-1}, the corresponding three vibrational frequencies may be close to 1340, 1140, and 760 cm^{-1}, or to 1340, 1300, and 1140 cm^{-1}. In the latter case the 760-cm^{-1} band may be attributed to the bending vibration of the CO_2^{2-} group of ketene.

It should be noted, however, that the number of bands assigned to compound V and presented in Table 1 is more than that anticipated. The appearance of extra bands in the 1356- to 1300-cm^{-1} region may be caused by Fermi resonance with some overtone or combination mode of low-frequency vibrations including out-of-plane and in-plane bending vibrations of the $C{=}C{=}O$ group, which for the ketene molecules H_2CCO are located at 528 and 433 cm^{-1} (*22*). The hypothesis of Fermi resonance is supported by the fact that after ^{13}CO adsorption the relative intensities of the shifted 1356- to 1300-cm^{-1} bands are not the same as those in the corresponding spectrum of $^{12}C^{16}O$. However, even if we did not take into account the shift values of the bands in this region, it was not possible to determine a plausible force field which reproduces the other shift values with an accuracy better than 3.5 cm^{-1}.

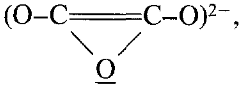
The structure of the ketene-containing compound proposed here differs from that supposed by the Turin group (*6*), who believed one carbon atom to be bound to a surface magnesium ion, so that the species in question should be a product of CO reduction. In our scheme the dioxoketene formation does not require electron transfer from any other atom but the surface oxygen ion incorporated in this structure and is not a result of CO disproportionation.

In the spectra of CO adsorbed on MgO, either obtained in Ref. (*6*) or studied here, the bands at 2109–2084, 1378–1355, 1320, and 1166 cm^{-1} are very close in their position and isotopic shifts to those of group V of CaO, and undoubtedly belong to several kinds of the same dioxoketene $C_2O_3^{2-}$ ions, which are more stable for MgO and exist on the surface at 300 K.

The bands at 1785 and 1260 cm^{-1} which arise on low-temperature CO adsorption on MgO and are absent in the spectrum of CaO are very much like those due to CO_2^- ions in their position and isotopic splitting. In fact, the bands at 1756 and 1221 cm^{-1} of $Li^+CO_2^-$ are shifted on ^{13}C substitution by 44 and 17 cm^{-1}, respectively (*15*, *20*), the shifts practically coinciding with those measured by us for the bands in question in the MgO spectrum (45 and 17 cm^{-1}). It should be noted, however, that bands at almost the same frequencies can be found in the spectra of bridged carbonates with a C–O bond order close to two (*23*).

Compound VI

Bands at almost the same wavenumbers as those attributed here to compound VI were observed earlier in the spectrum of CO adsorbed on CaO at 300 K by Coluccia and co-workers (*7*) who assigned them to the $(CO)_n^{2-}$ or $(C_nO_{n+1})^{2-}$ anions which have the form of five- or six-component rings containing carbon atoms. Our results, including those of isotopic substitution, do not argue with such an assignment, although because of the rather high halfwidth of the bands the presence of more than two carbon atoms in the composition of compound VI could not be proved by means of IR spectroscopy. The band at 1135 cm^{-1} can be attributed to the C–C vibration while the character of the isotopic splitting of the 1403- and 1234-cm^{-1} bands is more typical for the vibrations localised on C–O groups. We can thus conclude that compound VI contains at least two $C–O^-$ groups, bound via their C atoms.

Compound VI arises under conditions when compounds V are already present or begin to decompose on the surface. Dioxoketenes can thus be regarded as intermediates in the formation of compound VI. In fact, due to their high reactivity ketenes can interact with CO with the formation in our case of open or closed chains which will have the formula $(C_nO_{n+1})^{2-}$. The simplest cyclic structure of this series,  $(O–C{=}C–O)^{2-}$ (with the two C atoms bridged by an O below), isomeric with ketene, was already associated with the bands of group IV. All these structures contain one surface oxygen atom, but within the limits of experimental accuracy no influence of surface oxygen isotopic exchange on the position of compound VI bands was detected.

The bands of group VI can be alternatively attributed to the reduced compounds $(CO)_n^{2-}$, which can arise together with some oxidized forms of CO adsorption after CO association with compounds IV or V:

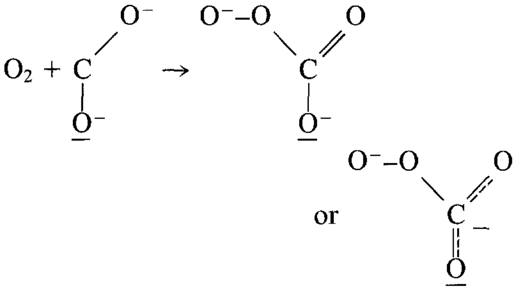
$$C_2O_3^{2-} + nCO \rightarrow (CO)_{n+1}^{2-} + (CO_2)_{ads}.$$

It is possible that in the result of such a reaction of CO disproportionation the oxygen atom, initially originating from the surface, turns out to be included in the oxidized products, denoted here as $(CO_2)_{ads}$. Then the reduced product will contain only the oxygen of the CO molecules, in accordance with the experimental data. Adsorption which can be attributed to the oxidized forms of adsorbed CO does actually arise in the 1650- to 1550 and 1350- to 1250-cm^{-1} regions simultaneously with the formation of compound VI. The position of these bands is characteristic for bidentate carbonates.

Products of CO Oxidation on CaO

Surface carbonate ions, undoubtedly account for the main part of the absorption arising after oxygen admission to the CO adsorbed on CaO when the oxygen-sensitive bands disappear. In these cases a band at 1050–950 cm^{-1} which belongs to the IR inactive symmetric stretching vibration of the carbonate ion, arising as a result of symmetry lowering for the ion on the surface, shows up. Bands in the 1700- to 1500-cm^{-1} region correspond to the antisymmetric stretching mode; however, some part of the absorption near 1600 cm^{-1} can be due to oxalate ions, which may also be a product of CO oxidation and may absorb near 1630 and 1315 cm^{-1}.

Oxidation of the CO_2^{2-} ions at 77 K gives rise to structure VII, which is not stable and disappears after heating the sample to 300 K. Two or three kinds of this species have slightly different, rather high-frequency bands in the 1850- to 1750-cm^{-1} region, characteristic of bridged surface carbonate ions which arise after CO_2 adsorption on some oxides (*23*). It is possible that for CaO such a structure appears after oxidation of the $(CO_2)^{2-}$ ions at 77 K and that after heating the sample it is transformed into bidentate (more usual for CaO) or some other form of carbonate ion. However, it is difficult to envisage that the interaction of an O_2 molecule with a single CO_2^{2-} ion at 77 K can cause oxygen dissociation and produce directly the carbonate ion. We believe that at low temperatures in the first stage of the oxidation the formation of an intermediate oxidized species with an undissociated oxygen molecule in a process such as



is much more favourable. The CO_4^{2-} species arising here should also have a high-frequency C–O vibration of the C=O bond or of the CO_2^- group bound to O_2^-, and compound VII can probably be associated with such a structure. The bands at 1838–1777 and 1257 cm^{-1}, in accordance with their isotopic shifts, may be attributed to the antisymmetric and symmetric vibrations of the carboxyl species, respectively. The best proof of the existence of such a structure would be the position and isotopic splitting of the band due to the O–O vibration after reaction with $^{18}O_2$, but this band, evidently, is much less intense and was not detected here.

The position of the compound VIII bands is typical for normal surface carbonate ions. The first kind, namely VIIIa, arises immediately after oxygen admission at 77 K, while the other, VIIIb, is a product of compound VII transformation. The isotopic shifts of these two kinds of carbonates are practically the same, although the frequencies are not completely identical. This means that there is some difference, perhaps, in the coordination of these two structures.

It is noteworthy that for the VIIIa structure no isotopic shift was detected after using $^{18}O_2$ as oxidizing agent, while the double shift caused by the carbonite oxygen substitution testifies that both the two oxygen atoms from the CO_2^{2-} ion remain in the formed carbonate. This fact can be explained if we assume that the molecular oxygen is used only as an acceptor of electrons, and one more oxygen ion is taken from the bulk of oxide to form the carbonate ion:

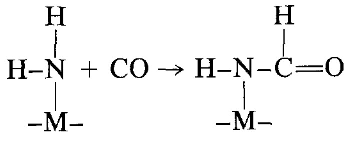
$$O_2 + \underline{CO_2^{2-}} + \underline{O^{2-}} \rightarrow$$
$$\underline{O_2^{2-}} + \underline{CO_2} + \underline{O^{2-}} \rightarrow \underline{O_2^{2-}} + \underline{CO_3^{2-}}.$$

Such a scheme without oxygen dissociation seems to be more favourable at low temperatures. Insensitivity of the VIIIb structure to O_2 substitution (with the exception of the slight shift of the 1586 cm^{-1} band) can be explained in the same way, if the decomposition of the hypothetical CO_4^{2-} compound occurs with detachment of the O_2^{2-} ion.

The position of the compound IX bands is also typical for carbonates, and the great number of bands above 1000 cm^{-1} indicates that at least three structures are present which probably have pairs of bands at 1665 and 1249, 1554 and 1308, 1394 and 1346 cm^{-1}. The most important difference between compounds VIII and IX is in the isotopic shifts. Practically all the compound IX bands are sensitive to substitution in the oxygen used for oxidation, which evidently becomes incorporated in the structure of the carbonate as well as the oxygen atoms of the oxidized compound III.

Mechanism of CO Transformations on Basic Oxides

Many different structures arising after CO adsorption on CaO and MgO either can be formed independently on different surface sites, or may appear one after the other in a single chain of transformations of the first product of CO interaction with a certain active site. Our attempt to poison some surface sites by adsorption of ammonia on MgO shows that neither carbonite nor the other products of CO chemisorption arise on samples with preadsorbed ammonia. In accordance with the work of the Turin group (*24*), the main product of CO adsorption in this case is formamide or its derivatives, formed by reaction with surface NH_2 groups,



$$\underset{-M-}{\overset{H}{H-N}} + CO \rightarrow \underset{-M-}{\overset{H}{H-N}}-\overset{H}{C}=O$$

or with preadsorbed ammonia molecules (*12*, *14*). In any case, ammonia molecules block all the sites for CO chemisorption.

By varying the pretreatment temperature of MgO and CaO samples we also tried to find conditions where only the sites responsible for *some* of the II–VI structures arise, but every time bands arose after CO adsorption *all* the compounds could be seen, and the only difference was in the overall intensity of the bands.

For thorium oxide, where the bands assignable to the CO_2^{2-} ions appear after CO adsorption at room temperature (*17*), spectra registered at 240 K reveal a double band at 2100–2091 cm^{-1}, accompanied by a group of bands below 1400 cm^{-1} (*25*), which can naturally be associated with the dioxoketene structure.

The data presented above assure us that there are no special sites responsible for the formation of the IV–VI compounds only; they are all products of CO interaction with the same basic oxygen ions which account for the structures II and III, the precusors of all the other compounds. The overall probable scheme of CO transformations on the surface of basic oxides is thus

$$\underline{O}^{2-} + CO \rightarrow \underset{\text{II, III}}{\underline{CO_2^{2-}}} + CO \rightarrow$$

$$\underset{\text{IV, V}}{\underline{C_2O_3^{2-}}} + CO \rightarrow \underset{\text{VI}}{\underline{(CO)_n^{2-}}} + \underset{\text{VIII}}{\underline{CO_3^{2-}}}$$

where the underlining indicates ions belonging to or adsorbed on the surface.

The first stage of CO adsorption which takes place at 77 K is the formation of carbonite CO_2^{2-} ions. At higher temperature these ions react with excess CO to form more complex dioxoketene or other (IV) structures. It is not clear whether all the kinds of CO_2^{2-} ions detected on CaO are equally reactive with respect to CO. Our preliminary data on CO adsorption on CaO with isotopically labeled IIa compounds did not reveal the appearance of the labeled products. Perhaps the IV and V structures are formed from the less stable IIb and III compounds. At even higher temperatures CO disproportionation takes place, resulting in the formation of the earlier established (5–7) reduced compounds and carbonate ions.

CONCLUSIONS

IR study of CO adsorption in a wide range of temperatures from 40 to 300 K provides a means to follow the mechanism of CO transformations on the surfaces of basic oxides. For CaO and MgO a great number of species were detected which have different thermal stability and reactivity with respect to oxygen. Application of isotopically substituted CO molecules, as well as adsorption of CO on an ^{18}O-enriched surface and comparison of the observed isotopic shifts with those calculated for the supposed structures, enables us to obtain information about the composition, structure, and force constants of these compounds.

It has been shown that the coordinatively unsaturated surface O^{2-} ions are the active sites of CO chemisorption on the surface of basic oxides. Metal ions evidently play a less important role of charge compensation and affect the surface oxygen basicity, which should depend on the coordination and the nature of metal ions.

The first product arising after CO admission either at 300 K or at low temperatures is the "carbonite" $(CO_2)^{2-}$ ion, which is the result of CO interaction with a surface O^{2-} ion. At temperatures higher than 100 K carbonite ions react with the excess of CO to produce dioxoketene $(O{=}C{=}CO_2)^{2-}$ ions. Further reactions with CO give rise to more complex compounds, both oxidized and reduced, in accordance with the data earlier obtained at 300 K (5–7).

Reversible interaction of CO with surface O^{2-} ions with the formation of CO_2^{2-} ions is responsible for the catalytic reaction of low-temperature homonuclear isotopic exchange of CO on the surface of basic oxides.

We suppose that the established mechanism of CO activation by oxygen ions is typical for different reactions on basic or alkali-promoted catalysts. In fact, for certain metals coadsorption of CO with alkali atoms produces species with CO vibrations at very low frequencies (*26*), close to those observed here for CO_2^{2-} ions. It is possible that for some of these systems CO really interacts with O^{2-} ions originating, for example, from CO dissociation, and the observed bands are due to the high-frequency vibration of the CO_2^{2-} structure.

Note added in proof: After the paper had originally been submitted for publication, new results were obtained (*27*) concerning CO adsorption on La_2O_3 in which the formation of CO_2^{2-} was proved also for this oxide by means of isotopic substitution. Also, in their reinvestigation of UV and IR spectra of CO adsorbed on CaO and MgO at 300 K, Garrone, Zecchina, and Stone (*28*) have likewise come to the conclusion that CO_2^{2-} is a precursor of more complex compounds and have suggested a detailed scheme of CO transformations which is in accordance with ours. Finally, a paper (*29*) has been brought to our attention in which a structure identical to our CO_4^{2-}, but bearing a single negative charge, was proposed on the basis of ESR study for a product of CO interaction with surface O_2^- ions on MgO.

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