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Infrared Study of Carbon Monoxide Adsorption on Calcium and Strontium Oxides

BY SALVATORE COLUCCIA,* EDOARDO GARRONE, EUGENIO GUGLIELMINOTTI AND ADRIANO ZECCHINA

Istituto di Chimica Fisica dell'Università di Torino, C.so M. d'Azeglio 48, 10125 Torino, Italy

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CO adsorption on CaO and SrO takes place, as on MgO, *via* a disproportionation reaction leading to both surface carbonates and unusual surface species with a complex vibrational spectrum in the low-frequency range. These are thought to be negatively charged CO polymers, the simplest ones being $(CO)_2^{2-}$. A strong electrostatic interaction between negative species and surface cations accounts for the marked dependence of the infrared signal on the lattice parameter of the solids. The increasing basicity along the series MgO, CaO, SrO causes: (i) a marked increase in the total adsorptive capacity; (ii) an increase in the relative population of polymers with respect to dimers; (iii) an increase in the importance of a Boudouart-like reaction upon desorption.

No infrared studies on the CO/CaO and CO/SrO systems have been carried out previously. In contrast, u.v.–visible reflectance studies on severely dehydrated CaO and SrO[1] have shown that CO chemisorption takes place with the formation of unusual species which have electronic transitions in the visible and near-u.v. This has been previously shown by i.r. spectra in the case of MgO.[2] The aim of this investigation is to use i.r. spectroscopy to obtain further information on the nature of these species and on the mechanism of their formation.

EXPERIMENTAL

The samples were prepared as follows. Specpure $CaCO_3$ and $SrCO_3$ (Johnson Matthey) were decomposed *in vacuo* to give CaO and SrO and then contacted with H_2O vapour to give $Ca(OH)_2$ and $Sr(OH)_2$. The hydroxides were then pelletted, slowly decomposed at 523 K *in vacuo* (1×10^{-4} N m^{-2}) in the i.r. cell and then outgassed up to 1073 K. After outgassing B.E.T. surface areas were *ca.* 110 m^2 g^{-1} (CaO) and *ca.* 6 m^2 g^{-1} (SrO).

In both cases pellets of *ca.* 30 mg cm^{-2} were used. The i.r. spectra were measured on a Beckman IR 12 spectrometer using a standard *in situ* silica cell. High-purity (Matheson) CO and O_2 were employed without further purification.

RESULTS

CO adsorption on CaO is strongly dependent on the pressure, whereas it is not significantly dependent on the time of contact with the gas phase. Fig. 1(*a*) and (*b*) show the i.r. spectra (subtracted from the background of the clean solid) which result when CO is dosed at increasing pressures. At low pressures [curve (*a*)] two absorption bands at 1485 and 892 cm^{-1} dominate the spectrum. Room-temperature outgassing at this stage almost eliminates the two absorptions and re-exposure to CO restores the original situation. At higher pressures [curve (*b*)] the spectrum becomes more

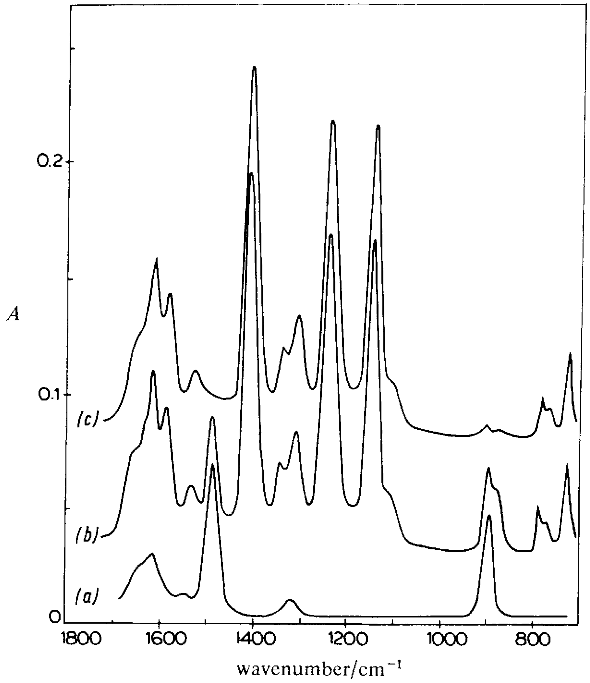


FIG. 1.—Spectra of CO adsorbed on CaO: (*a*) in the presence of 133 N m^{-2} CO; (*b*) in the presence of 6.65 kN m^{-2} CO; (*c*) after outgassing for 30 min at room temperature.

complicated and several bands at 1650 (sh), 1625 (sh), 1612 (m), 1578 (m), 1525 (w), 1485 (m), 1407 (s), 1338 (w), 1305 (m), 1230 (s), 1130 (s), 1100 (sh), *ca.* 990 (br), 892 (m), 880 (sh), 788 (w), 770 (w) and 725 (m) are observed. At the same time the intensities of the pair at 1485 and 892 cm^{-1} decrease. The sample colour is now yellow–orange. Curve (*c*) shows the effect of room-temperature outgassing: all bands remain unaltered except those at 1485 and 892 (the initial pair) and at 880 cm^{-1} which are strongly weakened. As the shoulder at 880 cm^{-1} behaves similarly to the 892 cm^{-1} band, we think that it is associated with the same type of species whose frequency is only slightly perturbed by the presence of the new groups formed on the surface by increasing the CO pressure. The same bands are always present on different samples, although the relative intensities of some of them may vary; this is sometimes particularly evident for the bands of the complex absorption at high frequencies (1700-1600 cm^{-1}).

Fig. 2 shows the effect of 473 K outgassing on the spectrum of the adsorbed species. Curve (*a*) is the spectrum of a CaO sample which, after CO adsorption, has been outgassed at room temperature; curve (*b*) is obtained after outgassing at 473 K. The bands at 1407 (s), 1230 (s), 1130 (s), 1100 (sh), 788 (w) and 725 (m) cm^{-1} disappear, thus showing that they belong to the same or similar species. At the same time the bands in the 1500-1700 and 1200-1400 cm^{-1} ranges are affected as some of the components show an intensity increase (1578, 1550 and 1305), whereas the intensities of others (1650 and 1625) decrease. Upon outgassing at 473 K the colour turns white.

Fig. 3 shows the effect of oxygen exposure on preadsorbed CO outgassed at room temperature. The main results are: (i) the disappearance of the bands at 1407, 1230,

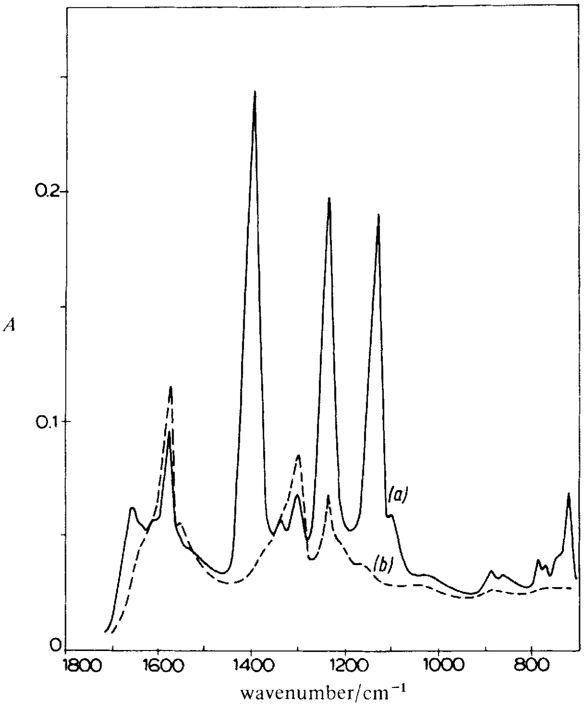


FIG. 2.—Spectra of CO adsorbed on CaO: (*a*) sample contacted with 6.65 kN m^{-2} of CO and then outgassed at room temperature for 30 min; (*b*) after outgassing at 473 K for 30 min.

1130, 1100, 788 and 725 cm^{-1} (at the same time the sample turns white); (ii) an increase in intensity of the absorptions in the 1500-1700 and 1400-1200 cm^{-1} ranges and at 990, 965, 890, 770 and 750 cm^{-1}. In another experiment a CaO sample which had previously been exposed to a low pressure of CO and which therefore showed only the bands at 1485 and 892 cm^{-1} was contacted with O_2. The result was the disappearance of these bands.

By summarizing the data of fig. 1-3 the following conclusions are firmly established: (i) the bands at 1407, 1230, 1130, *ca.* 1100, 788 and 725 cm^{-1} belong to the same oxygen-sensitive species (or family of similar species) which are responsible for the yellow-orange colour; (ii) the bands at 1485, 892 and 880 cm^{-1} are associated with a second oxygen-sensitive species having a partial transient character; (iii) most, if not all, bands in the 1500-1700 and 1200-1400 cm^{-1} ranges belong to several similar species whose concentrations grow in oxidizing conditions.

Fig. 4 shows the i.r. spectrum of CO adsorbed on SrO [spectrum (*a*)]. As in the previous case, the background spectrum of the clean solid has been subtracted. Several bands are observed at 1670 (sh), 1605 (m), 1530 (br), 1395 (sh), 1360 (s), 1310 (sh), 1150 (m), 1090 (m), 1045 (sh), 855 (sh), 830 (vw), 800 (w) and 770 (w) cm^{-1}. No changes are observed in this spectrum either on increasing the time of contact with the gas phase or by outgassing at room temperature. In the same figure the effect of oxygen exposure is illustrated [spectrum (*b*)]. The main results are: (i) the disappearance of the bands at 1360 (s), 1150 (m), 1090 (m), 1045 (sh), 830 (vw) and 800 (w) cm^{-1} which

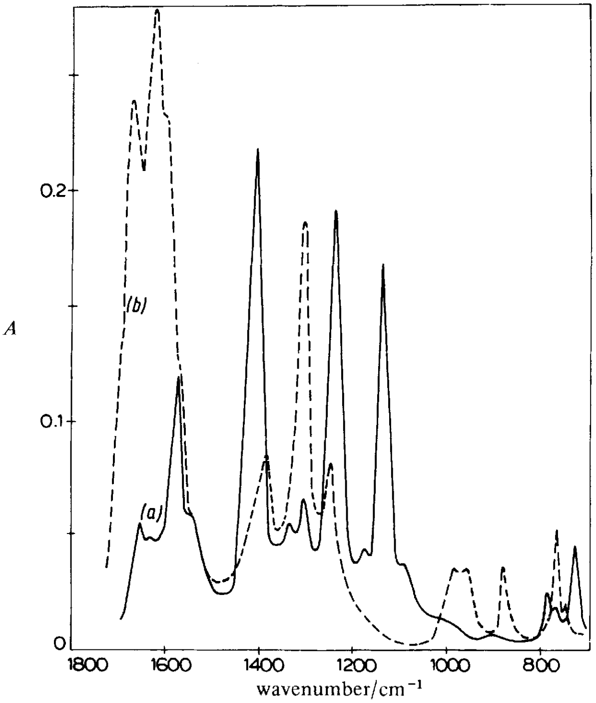


FIG. 3.—Effect of oxygen on CO preadsorbed on CaO: (*a*) sample contacted with 6.65 kN m^{-2} CO and then outgassed at room temperature; (*b*) after contact with 1.33 kN m^{-2} O_2.

are thus associated with one or more similar species; (ii) the increase in intensity of the absorptions in the 1500-1700 (1670, 1605, 1530), 1250-1400 (1395, 1310) and 900-750 (855, 770) cm^{-1} ranges. The colour of the sample is pale yellow after CO adsorption and turns white upon subsequent oxygen contact.

DISCUSSION

The i.r. spectra of CO adsorbed on CaO and SrO have a degree of complexity which is similar to that of CO on MgO.[2] As in the previous case the surface species can be divided into two main groups. The species of the former group are destroyed by oxygen at room temperature, whereas the species of the latter group, far from being destroyed by oxygen, grow when the oxygen-sensitive species are depleted. In table 1 the frequencies of the adsorbed species on MgO,[2] CaO and SrO are compared: species which behave similarly on the three oxides are labelled in the same way.

By analogy with MgO, the oxygen-sensitive species on CaO and SrO are divided into two sub-groups C and E: C species are characterized by several bands in the 1500-700 cm^{-1} range, while the E species exhibit a much simpler two-band spectrum. The absence of some species on CaO and SrO will be commented on later.

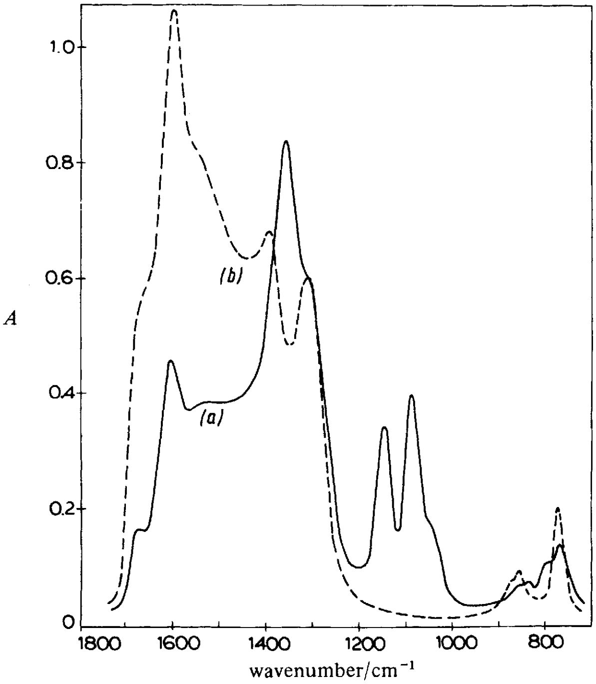


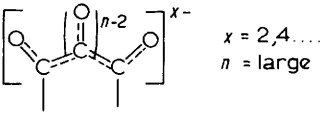
FIG. 4.—Effect of oxygen on CO preadsorbed on SrO: (*a*) CO preadsorbed on SrO; (*b*) after contact with 1.33 kN m^{-2} O_2.

TABLE 1.—SURFACE SPECIES UPON CO ADSORPTION ON ALKALINE-EARTH OXIDES (cm^{-1})

	species	MgO	CaO	SrO
oxygen-sensitive species	A	2200	—	—
	B	2064, 1318	—	—
	C	1480, 1275 1197, 1066	1401, 1230, 1130 1100, 788, 725	1360, 1150, 1090 1045, 830, 800
	D	2108-2084	—	—
		1358-1392	—	—
	E	1582-1548	1485, 892	—
		1160	—	—
oxygen-insensitive species	F	1600-1750	1500-1700	1500-1700
		1220-1280	1200-1350	1250-1350
		1010	990, 965, 890	855, 770
		—	770, 750	—

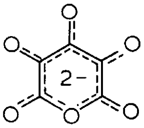
CALCIUM OXIDE: STRUCTURE OF THE OXYGEN-SENSITIVE SPECIES (C AND E)

Being characterized by 6 bands in the 1500-700 cm^{-1} range, the C species must have a more than diatomic character. The highest frequency mode is at 1407 cm^{-1}: hence C—O and/or C—C bond orders between one and two are strongly suggested, thus ruling out possible structures containing ketonic carbonyl groups.[1, 3] As a consequence, as in the MgO case,[2] a less-common structure must be taken into account. On MgO C species have been considered to be cyclic $(CO)_n^{x-}$ anions, in agreement with their simple i.r. spectrum,[2] with the low-frequency electronic transition observed by reflectance spectroscopy[1, 3] and with the low coverage.[2] On CaO the complexity of the i.r. spectrum (6 bands in the 1400-700 cm^{-1} range) and the higher coverage (*ca.* 6 times larger)[1] lead us to consider slightly different structures, *e.g.* anionic $(CO)_n^{x-}$ clusters with lower symmetry and/or a higher degree of polymerization. Possible structures range from linear chains [structure (*a*)] to non-symmetric cyclic CO clusters formed for instance by disordered condensation at high coverage of simpler fragments essentially symmetric in nature. As many arrangements of the CO units are possible within large resonance-stabilized anionic CO clusters, definite structures will not be given.



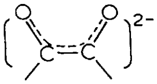
(*a*)

We note here that, on purely spectroscopic grounds, the same bands could also be consistent with anionic species *not* of the simple $(CO)_n^{x-}$ type. For instance six-membered charged cycles $(C_nO_{n+1})^{2-}$ [structure (*b*), $n = 5$] containing a surface oxygen atom in the ring, have a symmetry sufficiently lowered with respect to the six-membered $(CO)_n^{x-}$ symmetric analogues to justify the number of bands observed. An unambiguous choice between the two (or even more) different types of species briefly described above cannot be made by i.r. spectroscopy alone. As a consequence a definite hypothesis on the nature of the C species will only be given in the following on the basis of its consistency with the general patterns of the whole series of CO alkaline-earth oxide systems. The E species (as in the MgO case) are characterized by two bands in the 1600-800 cm^{-1} range which imply that more than diatomic species are necessarily involved. In order to make a reasonable hypothesis on their structure the following has to be taken into account: (i) the frequencies of the observed bands imply bond orders < 2; (ii) the surface concentration of the E species is a maximum in the initial stages of adsorption (low θ) and then decreases when the C structures are formed by increasing the CO pressure. Hence the E species must be considered as simplified versions of the C species and their partially transient nature may be understood by supposing that the C species can be formed from the simpler E ones by further CO insertion at high pressure. Due to the simplicity of the i.r. spectrum,



(*b*)

we propose the same structure as that already advanced in the MgO case, *i.e.* structure (*c*) similar to that of analogous $N_2O_2^{2-}$ aggregates already observed for the NO/MgO system.[4] The well-documented[1, 2] anionic nature of the C and E species on both CaO and MgO implies that the two oxides behave similarly toward CO adsorption. However, important differences must be pointed out: (i) CO adsorption is faster and more extensive on CaO than on MgO; (ii) the absence of bands in the 2000-2100 cm^{-1} range indicates that ketenic structures[2] with Ca^{2+}—C covalent bonds are either absent, or in much lower concentrations; (iii) depolymerization *in vacuo* of the C species (in the room-temperature to 473 K range) accompanied by E fragment formation does not occur on CaO, a different destruction pathway probably being favoured.



(*c*)

STRONTIUM OXIDE: STRUCTURE OF THE C SPECIES

These are characterized by six bands in the 1400-1200 cm^{-1} range which are easily explained on the basis of anionic aggregates with C—C and/or C—O bond orders less than two. As the CO coverage is very high (about one order of magnitude larger with respect to CaO)[1] it is even more difficult to ascribe the observed bands to a specific surface structure as several species can result from the chemical interaction of simpler fragments. With respect to MgO and CaO note that: (i) CO adsorption is instantaneous; (ii) ketenic structures are absent or in extremely low concentrations as on CaO; (iii) E-type species cannot be detected because of the complexity of the spectra. Their presence is documented by the u.v. measurements,[2] although it is plausible that their concentration is small.

It thus appears that in the whole series the overall activity is in the order MgO < CaO < SrO. This suggests that the basicity of the adsorbent plays a definite role in determining the total adsorptive capacity towards CO. Moreover, the increasing size of the cations renders less favourable the formation of cation–carbon partially covalent bonds: ketenic structures are found only on MgO, and E species become less probable on CaO and SrO because they require the polarizing effects of the cations.

MECHANISM OF FORMATION OF ANIONIC AND CARBONATE-LIKE SPECIES

As on MgO,[2] on CaO and SrO the formation of the bands associated with resonance-stabilized anions is invariably accompanied by the appearance of numerous absorptions in the 1700-1500, 1400-1200 and 900-800 cm^{-1} ranges. In each range several components are observed whose relative intensity changes slightly from one sample to the other. Due to the complexity of the situation, a detailed assignment will not be attempted. As these regions are typical of carbonate-like species with slightly different structures (organic, bidentate, monodentate, *etc.*)[5] the conclusion is drawn that anionic species and carbonate groups are formed simultaneously. Two possible explanations of this fact can be given: (i) the two types of species are formed in well-defined proportions during the same surface process; (ii) they are formed in separate processes occurring at different sites, the fairly constant intensity ratio observed on all samples being merely the consequence of a constant ratio between the number of the two types of sites.

The first hypothesis is more consistent with anionic structures of the $(CO)_n^{x-}$ type and the second one is more consistent with *b*-type structures. In fact the only simple reaction[1] describing the simultaneous formation of both types of species well is:

$$xO^{2-}+\left(n+\frac{x}{2}\right)CO \rightarrow \frac{x}{2}(CO)_3^{2-}+(CO)_n^{x-} \quad \begin{pmatrix} n=2,3,\dots \\ x=2,4,\dots \end{pmatrix} \tag{1}$$

which clearly shows that reduced $(CO)_n^{x-}$ and oxidized $(CO_3)^{2-}$ species must be formed together.

Vice versa, *b*-type species can be formed in a non-redox process at active O^{2-} sites

$$O^{2-}+nCO \rightarrow (C_nO_{n+1})^{2-} \tag{2}$$

without the formation of (oxidized) carbonate-like structures. However, as carbonate groups are adsorbed, they should come from the independent CO disproportionation reaction

$$O^{2-}+2CO \rightarrow C+CO_3^{2-} \tag{3}$$

occurring at different sites (an alternative reaction scheme leading to CO_3^{2-} group will be discussed later). By i.r. spectroscopy alone a choice between the two possibilities cannot be made. Hence the two reaction pathways must be examined from a more general point of view. Reaction (1) is more plausible for the following reasons: (i) reaction (1) readily explains all the i.r. manifestations on the basis of only one type of site, whereas reactions (2) and (3) require two types of site with fairly constant relative concentrations (which is less likely); (ii) on the basis of reaction (1) (which can be considered the first step in a disproportionation process) the Boudouart reaction occurring at higher temperatures can be easily understood (as discussed below). As shown in fig. 2, by heating CO-covered CaO *in vacuo* at 473 K the C and E complexes disappear completely while the surface carbonates remain (a few changes are observed in the relative intensity ratios of the individual components, as on MgO). This indicates that C species are destroyed without the formation of intermediate low polymers. The most obvious destruction pathway is

$$(CO)_n^{x-} \rightarrow \left(n+\frac{x}{2}\right)CO(g)+\frac{x}{2}C+\frac{x}{2}O^{2-} \tag{4}$$

leading to i.r.-inactive carbon and oxygen ions. By heating at higher temperatures the surface carbonates also disappear due to desorption of CO_2

$$CO_3^{2-} \rightarrow CO_2(g)+O^{2-}. \tag{5}$$

A different path can also be present

$$CO_3^{2-}+C \rightarrow 2CO+O^{2-} \tag{6}$$

which is certainly predominant on MgO as desorption studies have shown.[6]

By combining reactions (4) and (5) taken in the opposite direction with the Boudouart reaction

$$xCO \rightarrow \frac{x}{2}CO_2+\frac{x}{2}C \tag{7}$$

the overall mechanism (1) is obtained. This means that all the manifestations observed by i.r. and reflectance spectroscopy can be considered as due to the products of a Boudouart-like incipient disproportionation reaction.

From the above discussion the conclusion can be drawn that either linear [structure (*a*)] or cyclic charged CO polymers of the general form $(CO)_n^{x-}$ are responsible for most of the features observed in the spectrum of CO chemisorbed on alkaline-earth oxides. These species are formed, together with the carbonate-like species, through mechanism (1).

However, the variation in the relative intensities of the bands assigned to the polymeric species and the even higher variation of the $(CO_3)^{2-}$ bands indicate that slightly different surface species are bound to be present, although to a minor extent, and different mechanisms can be operative. This is confirmed by the fact that a fraction of O_2-sensitive species could be associated not only with bands at or below 1400 cm^{-1}, but also with a band at a much higher frequency (*ca.* 1650 cm^{-1}) (see fig. 2). A heterocyclic structure as shown in (*b*) could well be responsible for this band. In fact the effect of the more electronegative O^{2-} centre could tend to polarize the π-cloud away from one or more carbonyl groups which, as a consequence, would develop a greater double-bond character. Some contribution to carbonate-like species formation could also come through an independent mechanism from non-stoichiometric excess oxygen ions O^- thought to be present in alkaline-earth oxides prepared by thermal decomposition of parent hydroxides or carbonates[7-9]

$$2O^- + CO \rightarrow CO_3^{2-}. \quad (8)$$

NATURE OF THE ADSORBING SITES AND STRUCTURE OF THE ADSORBED SPECIES

From the previous discussion the conclusion has been reached that active sites contain reactive oxygen ions. Despite all the uncertainties concerning the real CO/O^{2-} stoichiometry of the chemisorption process (which derives from the uncertainty in n) it can be safely concluded (on the basis of the observed coverages) that the activities are in the order SrO > CaO > MgO. The very low value of θ (*ca.* 1.5%)[1] observed on MgO is an indication that only O^{2-} ions in exceptional surface situations, *i.e.* corner and/or kink positions,[1, 2] are sufficiently active to interact with gaseous CO. In contrast the much larger figures observed on CaO and SrO suggest that on these oxides surface O^{2-} ions in more normal surface configurations (*i.e.* edges and faces) can also react with carbon monoxide. This reactivity enhancement is a strong indication that basicity is one of the driving factors in the CO chemisorption and disproportionation process, the other one being the coordinatively unsaturated state of the O^{2-} ions. The complexity of reaction (1) leading to a few complex species adsorbed in vicinal positions implies that several ions (both positive and negative) participate in the process in a concerted way. As a consequence the adsorbing site must be imagined as an active patch containing not only reactive O^{2-}_{cus} ions but also suitably arranged positive ions whose main function is probably to act as counterions to the negative entities formed in reaction (1). When the positive counterions are small and hence the polarizing power is large (Mg^{2+}), polarized structures become favoured up to the limiting point that a better description of the adsorbed species is achieved in terms of covalent structures.

This fact explains why ketenic structures are abundant on MgO and why type E dimeric species are not favoured on SrO. From the previous considerations it appears that, due to the strong Coulombic interactions, there is a close relationship between the structure of the adsorbed species and the structure of the adsorbing patches. If, as in the CaO and SrO cases, the coverages are high enough to include a large variety of surface configurations, the description of the surface species in terms of well-defined structures will result in an excessive oversimplification. This consideration probably holds also for the MgO/CO system (even if the coverage is definitely smaller) and hence the symmetric structures already proposed must be considered more as useful models (which have homogeneous analogues)[10] than real entities.

COMPARISON BETWEEN I.R. AND U.V.-VISIBLE SPECTRA OF ADSORBED CO

The existence of a complete set of i.r. and u.v.-visible data[1,2] gives us the opportunity of comparing information derived from different spectroscopic sources. In particular we focus attention on the following observations: (i) electronic transitions of the C species move to higher frequencies on passing from MgO to CaO and SrO; (ii) the highest i.r. mode of the species moves gradually to lower values in the same sequence (the same behaviour is also shown by other bands but a band-to-band correlation cannot easily be made because different parent structures are probably involved). For the electronic transitions of the C species the following considerations have been made:[1] (i) they have a $\pi \rightarrow \pi^*$ character as their intensity and lattice-parameter dependences show; (ii) due to their composite structures the presence of families of similar species (instead of single species) is not excluded; (iii) the shift to higher frequencies is explained in terms of decreasing resonance stabilization on passing from MgO to SrO. The last conclusion apparently conflicts with the supposed increasing degree of polymerization of the C species (and hence of the size of the resonant systems) which should induce a shift in the opposite direction. Concerning the low-frequency shift of the first i.r. mode the only simple hypothesis which can be made is that, despite the uncertainties deriving from the possible presence of families instead of single species, the C—C and/or C—O bond orders decrease on passing from MgO to SrO. In order to conciliate these apparently conflicting conclusions (decreasing resonance stabilization, increasing size and decreasing bond orders) a first plausible explanation is that, due to the strong adsorbate–adsorbent Coulombic interactions, the length of the bonds is progressively increasing along the MgO–SrO series. In other words, along the examined series (for which the lattice parameter increases) the C species ‘expand’ in order to optimize the adsorbent–adsorbate interaction energy which thus appears as an extremely important fraction of the total species formation energy. Following this view, a small decrease in the resonance stabilization (which occurs when the bonds are lengthened or stretched in order to follow the expansion of the lattice parameter) is well compensated by the optimum match of the Coulombic forces between the increasingly ionic solids and the anionic C species. In this way the fairly constant stability to desorption at high temperatures of the C species in the MgO–SrO series gains a plausible explanation. The previous discussion is based on the assumption that stretched configurations in the parent compounds have lower i.r. modes and higher $\pi \rightarrow \pi^*$ transitions (because of the decrease in the *p* orbital overlap in the stretched configurations). Due to the peculiarity of the surface compounds under discussion and the lack of data concerning the energy level dependence upon expansion of bond length in similar compounds, we do not know if the ‘stretching’ effect alone is sufficient to explain the large shift in the electronic transitions. As a consequence the simultaneous presence of other factors influencing the electronic configuration in the same direction cannot be excluded. Among these, progressive changes in the anion structures along the MgO–SrO series (for instance from a cyclic to an open structure) or changes in the negative charge carried by each species cannot be excluded.

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