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Infrared Spectra of Carbon Monoxide, Carbon Dioxide, Nitric Oxide, Nitrogen Dioxide, Nitrous Oxide, and Nitrogen Adsorbed on Copper Oxide

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Infrared spectra of CO, CO_2, NO, NO_2, and N_2O adsorbed on silica supported CuO have been obtained over the temperature range of 30–250°C. Bands were observed at 2170, 2140, 1675, 1585, and 1350 cm^{-1} for CO; 2350 cm^{-1} for CO_2; 1890, 1605, 1575, and 1510 cm^{-1} for NO; 1740, 1585, 1520, 1490, 1265, and 745 cm^{-1} for NO_2; and 2220 cm^{-1} for N_2O. Efforts to obtain the spectrum for adsorbed N_2 were not successful. The spectrum for each adsorbed gas is interpreted in terms of the type and strength of bonding with the surface.

INTRODUCTION

The present study was performed as the first stage of an investigation into the mechanism and kinetics of the reduction of nitric oxide by carbon monoxide over a copper oxide catalyst. Since infrared spectroscopy was to be used to characterize the catalyst surface under reaction conditions, it was considered important to interpret first the spectra obtained for the individual adsorption of each of the reactant and product gases. Carbon monoxide, carbon dioxide, nitric oxide, nitrous oxide, and nitrogen were selected as adsorbates since all of these compounds were expected to be present in the gas phase under reaction conditions. Nitrogen dioxide was later added to this set as part of the effort to identify the spectral features observed for adsorbed nitric oxide. The temperature range chosen was 30 to 250°C, but only a single gas phase concentration was used for each adsorbate.

EXPERIMENTAL SECTION

The catalyst was prepared by slurrying a quantity of silica powder (Cab-O-Sil M-5) with an aqueous solution of cupric nitrate (Malinkrodt CP Grade). The proportions of silica and cupric nitrate were adjusted so that the final catalyst would contain approximately 9% of copper by weight. After stirring the solution to assure a good dispersion of the silica, the water was removed by freeze drying. This produced a dry fluffy pale blue powder.

The freeze-dried powder was next placed in a Pyrex tube heated by a clam shell furnace. The gas in the tube was evacuated by a diffusion pump and the powder was maintained at a temperature of 300°C and a pressure of approximately 10^{-6} Torr for a period of 24 hr. During this time the nitrate was decomposed leaving a brown-black powder as the final product. From a powder camera X-ray diffraction pattern the brown-black powder was identified as cupric oxide. The diffraction pattern also showed a fainter series of lines corresponding to metallic copper. Although a particle

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size for the cupric oxide was not determined, the breadth and faintness of the diffraction lines suggested the likelihood of small crystallites. An analysis of the copper contained in the final catalyst was obtained by dissolving a portion of the catalyst in a mixture of nitric and sulfuric acids and then electroplating the copper onto a platinum electrode. By this means it was ascertained that the catalyst contained 8.7% copper by weight.

For use in the infrared cell, the catalyst powder was pressed into a self-supporting disc. A second disc containing only silica was also formed for use as a reference. Each disc weighed 0.2 g and was 1 in. in diameter and 0.03 in. thick. A small copper–constantan thermocouple was imbedded into each disc for the measurement of the disc temperature. The thermocouples had lead wires 0.002 in. in diameter and beads 0.007 in. in diameter.

The infrared cell, shown schematically in Fig. 1, was built of 304 stainless steel. It consisted of a rectangular central chamber (1.5 × 0.5 × 7 in.) to contain the catalyst and reference discs and two conical channels to serve as passages for the sample and reference beams of the spectrometer. Each end of the channels was closed off by a potassium bromide window secured by a flange to a water-cooled slab. Viton O-rings were used to obtain a vacuum-tight seal between the windows and the slab. A flanged opening located at one end of the central chamber provided access into the cell. This opening was covered by a plate which supported a track onto which were mounted stainless steel holders for the catalyst and reference discs. The cover plate also contained feed throughs for the thermocouple leads.

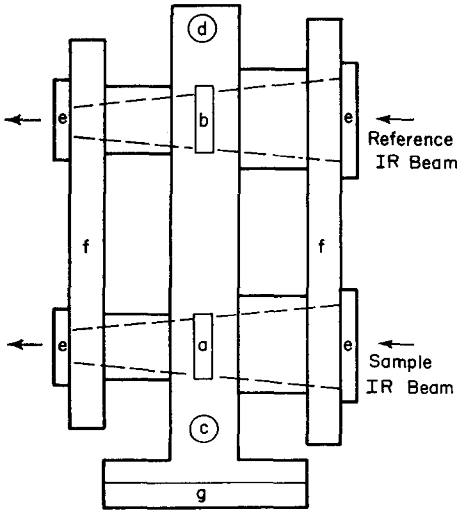

FIG. 1. Schematic of infrared cell: (a) sample disk; (b) reference disk; (c) gas inlet; (d) gas outlet; (e) KBr windows; (f) cooling channels; (g) cover flange containing thermocouple feed throughs.

The assembled cell fitted snugly into the sample compartment of a Perkin-Elmer 457 infrared spectrometer which was used to record the spectra. Gases were introduced into and taken out of the cell through ports located at the top of the rectangular chamber. When necessary the cell could be evacuated by connecting one of these ports to a diffusion pump and liquid nitrogen trap. Heating of the gas and discs was accomplished by two cartridge heaters located in the top and bottom walls of the central chamber.

The infrared spectra of gases adsorbed on cupric oxide were recorded with the catalyst disc placed on the sample side of the cell and the silica disc placed on the reference side. This mode of operation provided several advantages. First, by using two discs containing essentially the same amount of silica, the spectrum of silica could be subtracted from that of the sample providing an essentially flat base line. Secondly, the presence of the silica disc in the reference side of the spectrometer balanced the transmission of light on both sides of the spectrometer. Because of this it was possible to cancel out the gas phase spectrum and to record the adsorbed phase spectrum in the presence of the adsorbing gas. Finally, because the silica and catalyst discs were both exposed to the same gas, it was possible to subtract out the spectrum of gas adsorbed on the silica. Consequently, only the spectrum of gas adsorbed on the catalyst was recorded.

The experimental procedure used for each gas was the same. Prior to introducing the adsorbing gas the catalyst disc was exposed to a flow of helium containing 5% nitric oxide at 200°C for a period of about 3 hr. The cell was then evacuated and maintained at 130°C and a pressure of 10^{-6} Torr overnight. For those experiments in which CO_2, N_2O, and N_2 were adsorbed a number of runs were performed in which the catalyst disc was pretreated with 5% of carbon monoxide at 200°C prior to evacuation. To initiate a run, the vacuum was broken with a flow of helium and the temperature was adjusted to the desired level. At this time the adsorbate gas was added to the flow of helium so as to give an adsorbate concentration of 5 to 7%. The flow of helium plus adsorbate was continued until a steady state spectrum was obtained. At the end of the run the cell was evacuated and the disc was subjected to the appropriate pretreatment.

RESULTS

Adsorption on Silica

Prior to initiating work with the catalyst disc a series of experiments were performed with a disc of pure silica placed on the sample side of the reactor. The purpose of these experiments was to determine whether any of the gases to be studied would adsorb on the silica catalyst support, thereby producing a spectrum not associated with the catalyst. For these experiments the adsorbate concentration was held at 12% and the temperature was varied from 30 to 230°C.

The introduction of either NO or N_2 into the cell failed to produce any spectral features which could be observed above the background. Carbon monoxide produced a single band at 1725 cm^{-1} for adsorption temperatures between 30 and 75°C. Above 75°C this band could no longer be observed. When either CO_2 or N_2O was present in the cell the spectrum exhibited two or more inverted bands. These were located at 2350 and 670 cm^{-1} for CO_2 and at 2220, 1290, and 590 cm^{-1} for N_2O. The significance of these bands and their influence on the interpretation of the spectra observed with two discs is discussed below.

Adsorption on Copper Oxide

Below 150°C, the adsorption of carbon monoxide yields spectra like those shown in Fig. 2. The principal features of these spectra in Fig. 2 are a sharp band at 2140 cm^{-1}, an inverted band at 1725 cm^{-1}, and three broad bands centered at 1675, 1585, and 1350 cm^{-1}, respectively. The bands at 1725, 1675, and 1350 cm^{-1} are very sensitive to temperature and cannot be observed in the spectra recorded at temperatures above 33°C. Of the two remaining bands the one at 1585 cm^{-1} decreases more rapidly with increasing temperature and is no longer observable at temperatures above 150°C. A slight shift of the band downscale can

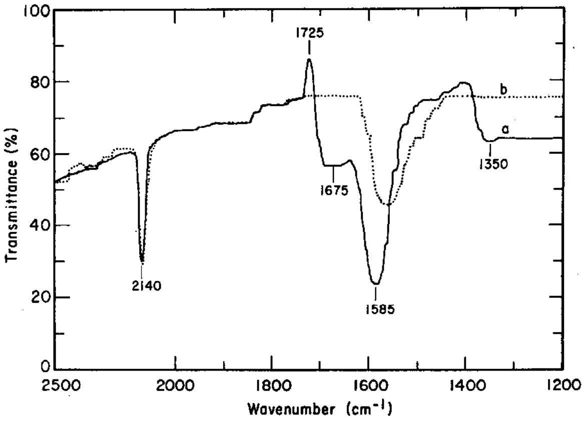

FIG. 2. Infrared spectrum of adsorbed CO: CO partial pressure = 0.05 atm; (a) T = 33°C; (b) T = 96°C.

also be observed as the temperature is raised.

The intensity of the band at 2140 cm^{-1} decreases slowly with increasing temperature and above 167°C a new band appears at 2170 cm^{-1}. This sequence is shown in Fig. 3. As can be seen the new band grows as the temperature is increased to 186°C, becoming more intense than the band at 2140 cm^{-1}. With a further increase in the temperature to 196°C both bands are strongly attenuated.

Figure 4 illustrates the spectrum of adsorbed carbon dioxide. Only a single broad band can be observed centered at 2350 cm^{-1}. The band is quite weak but shows a definite increase in intensity as the temperature is raised from 42 to 224°C. A pair of inverted bands centered at 2400 and 2290 cm^{-1} can also be observed. No differences in the spectrum are produced by pretreating the catalyst disc with carbon monoxide rather than nitric oxide.

The spectrum of adsorbed nitric oxide is shown in Fig. 5. A total of four bands can be identified which appear at 1890, 1605, 1575, and 1510 cm^{-1}. As the temperature is increased the intensity of all four bands is diminished. The three overlapping bands occurring at 1605, 1575, and 1510 cm^{-1} appear to behave as a group and are somewhat more sensitive to temperature than the band at 1890 cm^{-1}. Above a temperature of 152°C these bands are no longer discernible.

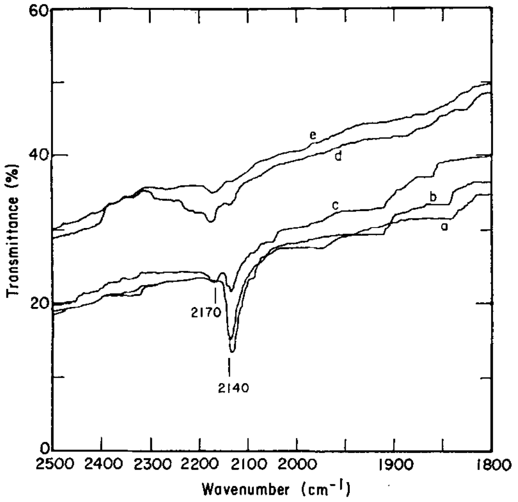

FIG. 3. Infrared spectrum of adsorbed CO: CO partial pressure = 0.05 atm; (a) T = 125°C; (b) T = 140°C; (c) T = 167°C; (d) T = 186°C; (e) T = 196°C.

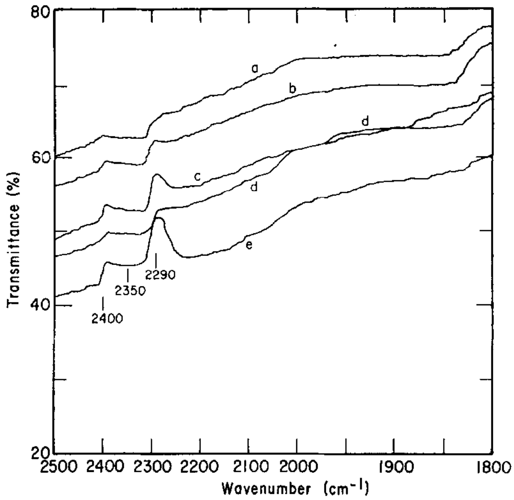

FIG. 4. Infrared spectrum of adsorbed CO_2: CO_2 partial pressure = 0.08 atm; (a) T = 292°C; (b) T = 224°C; (c) T = 152°C; (d) T = 122°C; (c) T = 104°C.

The spectrum of adsorbed nitrogen dioxide was obtained as part of an effort to deduce the identity of the bands appearing between 1650 and 1400 cm^{-1} in the spectrum of adsorbed nitric oxide. These spectra are

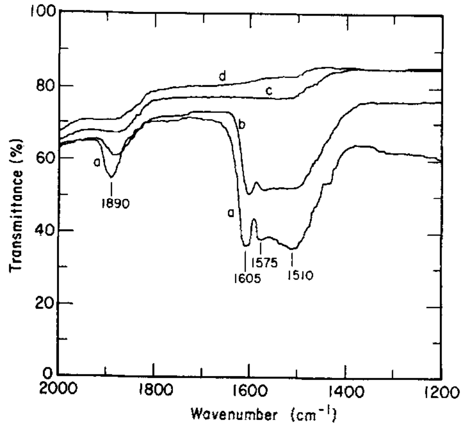

FIG. 5. Infrared spectrum of adsorbed NO: NO partial pressure = 0.05 atm; (a) T = 33°C; (b) T = 82°C; (c) T = 152°C; (d) T = 201°C.

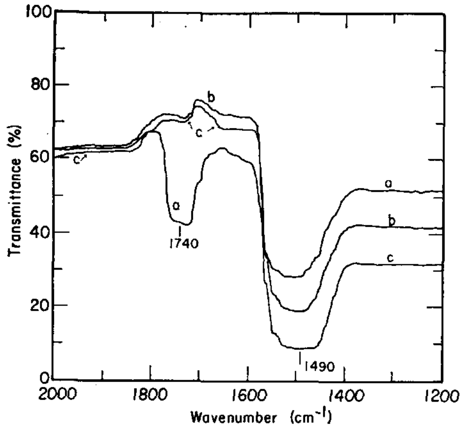

FIG. 6. Infrared spectrum of adsorbed NO_2: NO_2 partial pressure = 0.06 atm; T = 35°C; (a) t = 2 min; (b) t = 12 min; (c) t = 32 min.

shown in Figs. 6 and 7. Figure 6 illustrates that the initial adsorption of nitrogen dioxide at 35°C produces two broad bands at 1740 and 1490 cm^{-1}. As time progresses the band at 1740 cm^{-1} diminishes in intensity and the band at 1490 cm^{-1} grows. Increasing the temperature to 125°C causes the band at 1740 cm^{-1} to become more intense and the band at 1490 cm^{-1} to be shifted to 1520 cm^{-1} and greatly reduced in intensity. These changes may be seen in Fig. 7. A further increase in temperature to 230°C causes the band at 1740 cm^{-1} to be diminished and new bands to appear at 1585, 1265, and 745 cm^{-1}.

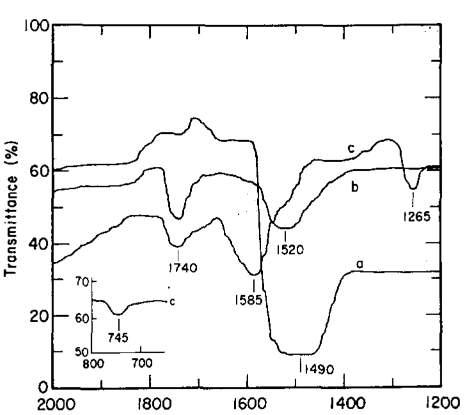

FIG. 7. Infrared spectrum of adsorbed NO_2: NO_2 partial pressure = 0.06 atm; (a) T = 35°C; (b) T = 125°C; (c) T = 230°C.

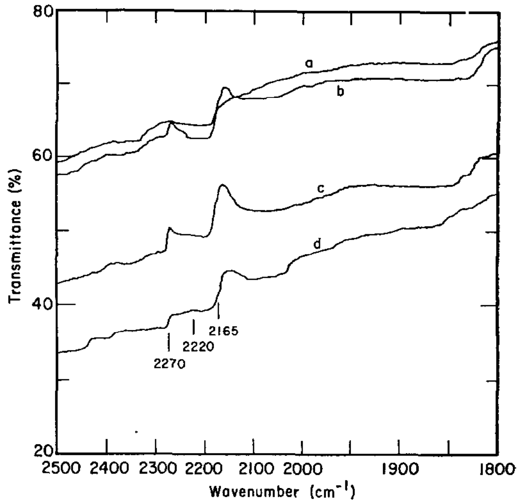

FIG. 8. Infrared spectrum of adsorbed N_2O: N_2O partial pressure = 0.08 atm; (a) T = 38°C; (b) T = 125°C; (c) T = 187°C; (d) T = 225°C.

Figure 8 shows the spectrum for adsorbed nitrous oxide. The only features observed are a broad band centered at 2220 cm^{-1} and two inverted bands at 2270 and 2165 cm^{-1}. The intensity of the bands increase with increasing temperature. Both of these characteristics are similar to those observed for carbon dioxide. Here too the pretreatment with carbon monoxide does not alter the spectrum.

Efforts made to observe the spectrum of nitrogen adsorbed on copper oxide were not successful. Despite a wide variation in the gas phase concentration of nitrogen, the temperature of the disc and the type of pretreatment, no bands could be observed.

DISCUSSION

Adsorption on Silica

Based upon the studies performed with a single silica disc it is possible to conclude that neither NO nor N_2 adsorbs on silica to a detectable extent. Similarly, the adsorption of CO cannot be observed for temperatures above 75°C. The inverted bands observed in the presence of either CO_2 or N_2O correspond very closely in their position to the bands for gaseous CO_2 (2349 and 667 cm^{-1}) and N_2O (2224, 1286, and 589 cm^{-1}). The reason that these bands are inverted is related to the greater amount of radiation which passes through the reference side of the cell compared to the sample side. This situation results from the fact that there is no compensation in the reference beam for the attenuation in the sample beam caused by the absorption of radiation in the silica. Consequently, the absorption of radiation by the gas in the two beams is not identical. Since CO_2 and N_2O are strong infrared absorbers, this imbalance produces a gas phase spectrum which is inverted. The interference of these gas phase bands with the observations of CO_2 and N_2O adsorbed on copper oxide is noted below.

Adsorbed CO

Whereas a large number of studies have been made of the infrared spectrum of carbon monoxide adsorbed on copper, very few have been made with copper oxide. The vibrational frequencies for the C–O bond reported in these studies are summarized in Table 1. As can be seen, the frequency of CO adsorbed on copper lies in the vicinity of 2110 cm^{-1}. Adsorption on copper oxide shifts the vibrational frequency upscale towards that of gaseous CO, 2143 cm^{-1}, and Gardner and Petrucci (*10*) have even observed a weak band at 2173 cm^{-1}.

Based upon the information reported in Table 1 it is possible to conclude that the bands at 2140 and 2170 shown in Figs. 2 and 3 are due to CO adsorbed on copper oxide and that there is no evidence for the adsorption of CO on metallic copper. Since the band at 2140 cm^{-1} lies very close to that of gaseous CO it suggests that the electronic structure of the corresponding adsorbed species is similar to that of gaseous CO. By contrast the band at 2170 cm^{-1} corresponds more closely to that for gaseous CO^+ which occurs at 2184 cm^{-1} and suggests that the species contributing to the absorption at 2170 cm^{-1} may carry a partial positive charge.

TABLE 1

POSITION OF INFRARED BANDS OBSERVED FOR CO AND CO_2 ADSORBED ON Cu AND CuO

Substrate	Gas	Frequency cm^{-1}	Ref.
Cu/SiO_2	CO	2120	(*1*)
Cu/SiO_2	CO	2120	(2)
		2100	
Cu/Al_2O_3	CO	2110	(*2*)
Cu/SiO_2	CO	2110	(*3*)
Cu/SiO_2	CO	2130	(*4*)
Cu/SiO_2	CO	2110	(*5*)
Cu/Al_2O_3	CO	2110	(*5*)
Cu film	CO	2105	(*6*)
Cu film	CO	2105	(*7*)
Cu film	CO	2110	(*8*)
Cu film	CO	2105	(*9*)
Cu/SiO_2	$CO + O_2$	2115	(*3*)
		1520	
		1375	
CuO/SiO_2	CO	2173	(*10*)
		2127	
		2000	
CuO/SiO_2	CO	2136	(*4*)
CuO/Cu film	CO	2135	(*9*)
CuO/SiO_2	CO_2	2360	(*11*)
		1680	
		1565	
		1500	
		1445	
		1360	
		845	

The nature of the interaction between adsorbed CO and copper oxide can be interpreted further in terms of Blyholder's theory (*12*) of the bonding between CO and transition metals. According to this theory a metal *d*, a carbon *p*, and an oxygen *p* orbital are combined to form a π-electron system consisting of three molecular orbitals. The orbital which is lowest in energy is bonding for both the carbon–metal and carbon–oxygen bonds and will be filled. The highest energy orbital is antibonding for both bonds and will be empty. The remaining orbital of intermediate energy is bonding for the carbon–metal bond and antibonding for the carbon–oxygen bond. The extent of filling of this orbital depends upon the competition for charge between this orbital and the orbitals of atoms surrounding the metal atom under consideration. Since this orbital is antibonding for the carbon–oxygen bond, increasing the charge in it will decrease the carbon–oxygen bond strength. The resulting model predicts that the infrared absorption frequency for C–O stretching will increase as charge is removed from the orbital of intermediate energy.

Application of Blyholder's model to the bonding of CO to the metals of the first transition series leads to the expectation of an increase in vibrational frequency as one moves from vanadium to copper. This shift is a result of the decrease in energy of the metallic *d*-orbitals. As the energy of the metal decreases, the competition between metal orbitals and the middle energy metal–carbon–oxygen molecular orbital causes a decrease of charge in this orbital. Since the latter orbital is antibonding with respect to the C–O bond, a decrease in its population causes an increase in the vibrational frequency of the C–O bond. An experimental verification of the qualitative features of the model have been given by Blyholder and Allen (*13*).

In view of Blyholder's model it is possible to propose that the vibrational frequency for CO adsorbed on a particular metal site will depend upon the nature of the bonding between the metal and its nearest neighbors. If one considers the conversion of the metal to its oxide, the metallic center becomes a positive ion whose nearest neighbors are oxygen anions. Under these circumstances the electrons of the metal *d*-orbitals are drawn away more strongly than if the metal site were surrounded by other metal atoms. By this reasoning it is possible to conclude that the availability of *d*-orbital electrons for participation in the π-bonding system will be reduced in the oxide relative to what it is in the parent metal. This reasoning would explain the increase in the vibrational frequency of CO adsorbed on copper oxide compared to metallic copper. The observation of two bands for chemisorbed CO in the present work suggests that the CO is bound to copper ions differing in their ability to contribute *d*-electrons.

The inverted band at 1725 cm^{-1} observed in Fig. 2 can be attributed to CO adsorbed on silica. This assignment was verified by adsorbing CO on a single disc of pure silica. The temperature dependence of the band intensity was identical to that described earlier. The inverted shape of the band indicates that there exists a slight imbalance in the amount of CO adsorbed in this manner between the reference and sample discs.

The remaining bands occurring between 1700 and 1300 cm^{-1} have not been described previously for CO adsorbed on copper oxide but are similar to those reported for other metal oxides (*14*). The three bands at 1675, 1585, and 1350 cm^{-1} also bear a great deal of resemblance to the bands observed by Amerikov and Kasatkina (*11*) for the adsorption of CO_2 on copper oxide. In that work the bands located at 1680, 1565, and 1360 cm^{-1} were attributed to bicarbonate, carboxylate, and carbonate species, respectively. The disappearance of the bands in the 1700–1300 cm^{-1} region at elevated temperatures as seen in Fig. 2 indicates that the oxygenated CO species are easily decomposed.

Adsorbed CO_2

The broad peak centered at 2350 cm^{-1} seen in Fig. 4 can be assigned to CO_2 bound to copper oxide. As is noted in Table 1 a similar peak has been observed by Amerikov and Kasatkina (*11*). Since the band is weak and occurs at essentially the gas phase vibrational frequency, 2349 cm^{-1}, it is possible to conclude that CO_2 is only weakly bound to copper oxide. The inverted peaks at 2400 and 2290 cm^{-1} seen in Fig. 4 are due to the incomplete cancellation of the spectrum of gas phase CO_2.

Adsorbed NO

The band at 1890 cm^{-1} appearing in the spectra shown in Fig. 5 is only slightly displaced upscale from that for gaseous NO (1876 cm^{-1}). From this it is possible to conclude that the N–O bond is not significantly perturbed by adsorption and that the M–N bond is relatively weak. Based upon Roev and Alekseev's (*15*) classification of the absorption frequencies for adsorbed NO one is led to conclude further that the adsorbed species is either $M^-{:}NO^+$ or $M^-{=}NO^+$ in which M might represent Cu, Cu^+, or Cu^{2+}. Since there have been no previous studies of the spectrum of NO adsorbed on either Cu or Cu_2O it is not possible to assign a unique identity to the adsorption site at this time. It is significant to note, however, that molecular orbital calculations of the bonding between NO and the first row transition metals performed by Blyholder and Allen (*16*) and by Roev and Zasuha (*17*) do predict that the M–N bond is weakest and the N–O bond is strongest for NO complexes formed with copper.

The remaining bands in the spectrum of adsorbed NO which occur at 1605, 1575, and 1510 cm^{-1} are more difficult to assign. If one assumes that either one or more of these bands is due to NO adsorbed on a metallic site, then one must conclude according to Roev and Alekseev's classification (*15*) that the surface structure is M^+NO^-. However, the absence of any prior observations of an adsorbed nitrosyl ion makes this assignment rather tenuous.

A more plausible interpretation of the bands present below 1600 cm^{-1} is that they are due to an interaction of NO with oxygen sites present on the copper oxide surface. Although Roev and Alekseev (*15*) claim that adsorption in this form does not occur on other transition metal oxides, we believe that such structures cannot be excluded. Thus the band at 1605 cm^{-1} could be attributed to a covalently bonded nitrate or nitrite group (*18*), whereas the bands at 1575 and 1510 cm^{-1} could be associated with monodentate and bidentate nitrato structures. The latter two structures are also present in the spectrum of adsorbed NO_2, which suggests the additional possibility that the corresponding bands may be due to the adsorption of NO_2 present as an impurity in the NO. Two points would argue against this last interpretation. The first is that no NO_2 could be found in a gas chromatogram of the NO used for adsorption. The second point is that the intensities of the infrared bands in the region of 1600 to 1400 cm^{-1} decrease as a single group with increasing temperature and at a rate which is consistent with the decrease in intensity of the band at 1890 cm^{-1}. Both of these observations suggest that the bands present in the spectrum of adsorbed NO are totally due to NO.

Adsorbed NO_2

The spectra for adsorbed NO_2 seen in Figs. 6 and 7 exhibit a band at 1740 cm^{-1} whose position is independent of temperature and one or more bands at lower frequencies whose positions are dependent upon the adsorption temperature. Through an examination of the spectra of many nitrogen oxides and nitrogen–oxygen complexes (*19*) we have concluded that the band at 1740 cm^{-1} can best be assigned to N_2O_4 which in the gas phase exhibits a band at 1712 cm^{-1}. Figure 6 shows that extended contact of NO_2 with the surface causes a band to appear at 1490 cm^{-1} which grows at the expense of the band at 1740 cm^{-1}. This second band can be assigned to a monodentate nitrato structure on the basis of Blyholder and Allen's (*18*) interpretation of the spectra of NO_2 adsorbed on Ni and Fe. When the temperature is raised to 125°C the band at 1490 cm^{-1} is shifted to 1520 cm^{-1}. A further increase in temperature to 230°C causes an additional shift of the 1490 cm^{-1} band to 1585 cm^{-1} and the appearance of bands at 1265 and 745 cm^{-1}. The positions of these latter four bands correspond rather closely to those observed for bidentate nitrato structures which occur at 1565–1500, 1290, 1020, 790, and 770 cm^{-1} (*19*).

Adsorbed N_2O

The single band at 2220 cm^{-1} seen in Fig. 8 can be immediately identified as adsorbed N_2O. Because the band intensity is weak and the band is not significantly shifted from its position for gaseous N_2O, 2224 cm^{-1}, it is possible to conclude that N_2O is not strongly adsorbed on copper oxide. Here, as in the case of CO_2, the inverted bands present at 2270 and 2165 cm^{-1} are due to an incomplete cancellation of the gas phase spectrum of N_2O.

CONCLUSIONS

Based upon the results of the present study we may conclude that the adsorption of CO, CO_2, NO, or N_2O on copper oxide yields at least one surface structure whose vibrational frequency is very close to that for the molecule in the gas phase. In the case of CO_2 and N_2O, which are weakly adsorbed, this is the only structure formed. The adsorption of CO near room temperature produces in addition a series of oxygenated species, while adsorption above 160°C produces a second linear structure which is presumed to carry a partial positive charge. For NO there is evidence that a part of the adsorbed molecules are present in the form of nitrate, nitrite, or nitrato structures. The adsorption of NO_2 confirms the possibility of forming nitrato structures on the surface of copper oxide. Finally, it should be noted that no evidence can be found for the adsorption of N_2 on copper oxide.

ACKNOWLEDGMENT

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