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Adsorption of CO_2, COS and CS_2 on Manganese Films

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Infrared, mass spectral and volumetric techniques have been used to examine the interaction of CO_2, COS and CS_2 with an evaporated manganese surface. CO_2 dissociated on the surface to give gas phase CO and an adsorbed CO_3 complex with infrared bands at 1580, 1305, 1050, and 825 cm^{-1} indicating a bidentate attachment of the complex. COS dissociates to give gas phase CO and, simultaneously, leave a sulfided surface. In neither of the cases of CO_2 or COS is chemisorbed CO found, and this is as expected for the former case since it has been found that CO_2 will displace chemisorbed CO on a manganese surface, while CO will not displace chemisorbed CO_2. Our evidence indicates that CS_2 is adsorbed dissociatively on the surface.

INTRODUCTION

In the effort to understand catalysis and surface chemistry, investigations of bond breaking and formation at metal surfaces by simple molecules have been carried out. Carbon dioxide is an appropriate choice for study because it is a relatively simple molecule and one of the expected products of dissociation is CO, whose adsorption has received considerable attention already. Infrared spectroscopy indicates that CO adsorbs readily on a wide variety of metals without dissociation (*1, 2*). The adsorption of CO_2 on Ni has been studied by several workers with varying results. Initially, the dissociative adsorption of CO_2 at 100°C to produce adsorbed CO on Ni was reported by Eischens and Pliskin (*3*). At 25° they reported no such dissociation since no infrared band for adsorbed CO was observed but rather the formation of adsorbed CO_2 and a monodentate CO_3 structure was proposed on the basis of infrared bands at 1390, 1410, 1560 and 1640 cm^{-1}. The silica support for their Ni cuts off radiation below 1350 cm^{-1}. In a later paper (*4*) they report CO_2 dissociation on Ni to give chemisorbed CO at 25°. Hardeveld and Hartog (*5*) found that CO_2 dissociated on their silica-supported Ni at 25° to give adsorbed CO and proposed that CO_2 adsorbed on a surface oxygen atom on the basis of a band at 1560 cm^{-1}.

Little (*1*) has reviewed some of the complications resulting from making assignments for adsorbed CO_2 on metals when only a limited portion of the spectrum has been obtained and has suggested the necessity and value of having the entire infrared spectral region available in order to make meaningful structural assignments for the final adsorbed species. Using a wide spectral range technique it has been shown that CO and oxygen on a Ni surface produce a bidentate CO_3 species whose structure is indicated by the presence of four infrared bands at 1560, 1330, 1040 and 830 cm^{-1} (*6*). This assignment based on four bands does cast some doubt on the structures for adsorbed CO_2 assigned by the previous workers based on their limited spectral ranges.

In this paper the results of using infrared, mass spectral and volumetric techniques to study the interaction of CO_2, COS, and CS_2 with a manganese surface are presented. These results have significance with regards to present day attempts to convert carbon monoxide and other pollutants to

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carbon dioxide by metallic catalysts in that very little consideration has been given to the oxidation products. The possibility of the converted products (in this case CO_2) reacting with the catalyst has been given little attention and in many instances, such reactions could be responsible for deactivation of the catalyst, especially if the reaction products decompose, or are preferentially adsorbed, on the catalyst rather than the reactants. Also, considering the results of the homologous series, CO_2, COS and CS_2 reacting with evaporated manganese gives indication of a possible mechanism for the deactivation of the manganese by sulfiding of the surface.

EXPERIMENTAL

The wide spectral range experimental technique, which has been used with a great deal of success in past experiments and described in detail elsewhere (7) consists of evaporating Mn from an electrically heated tungsten filament in the presence of a small pressure of helium. The metal particles formed in the gas phase deposit in a hydrocarbon oil film on the salt windows of an infrared cell. The gas to be studied is then admitted to the cell, and the spectrum of the chemisorbed species is obtained. Five minutes of pumping has been found sufficient to remove all spectra due to gas-phase molecules. Infrared spectra were taken immediately after the evaporation, after 40 Torr of either CO_2, COS, or CS_2 had been added to the cell, after the reactant gas had remained in the cell for 2–3 hr, and after the cell had been evacuated for periods of up to 30 min.

Volumetric measurements in a different apparatus were made to determine the relative amounts of the reaction gases that would adsorb on freshly evaporated manganese films. A known amount of manganese (determined by weighing the filament before and after the evaporation) was evaporated into a 250 ml oil free bulb attached to a vacuum system with a dosing arrangement. By this arrangement, known amounts of reactant gases could be successively introduced into the bulb containing the evaporated manganese film while continuously monitoring the pressure of the gas over the film. By knowing the volume of gas in each dosing increment and from the previously determined expansion ratio of the gas into the clean evacuated bulb with no evaporated metal, the amount of gas adsorbed per gram of evaporated manganese could be readily determined. All pressure measurements were made by a model 3294 LKB Autovac Gauge.

The nature of the gaseous reaction products formed by the interaction of CO_2, COS, and CS_2 with evaporated manganese films were determined by mass spectrometry. Determinations were made for samples which had been evaporated into an oil film as described and also for samples that were evaporated without the presence of the oil. Carbon dioxide, carbonyl sulfide, or carbon disulfide gas was introduced into the system before and after the evaporation, and the mass spectra were recorded using an E.A.I. Quad 150 mass spectrometer.

Carbon dioxide was obtained in the solid form and further purified by distilling three times from liquid air cooled traps and discarding the first and last portion of each distillation by pumping on the system. Carbonyl sulfide was obtained from K & K Laboratories, Inc., and distilled three times from liquid air cooled traps in the manner just described for CO_2. Carbon disulfide was obtained from Fischer Scientific Co. as reagent grade, and all dissolved gases which might have been present were removed by repeated freeze–thaw cycles with pumping. Manganese metal was obtained from E. H. Sargent Co. as small carbon free pieces, and was used as supplied until just before the evaporation at which time the metal was fused to a tungsten filament.

The infrared spectra were recorded on a Perkin–Elmer Model 21 spectrometer equipped with a sodium chloride prism and an ordinate scale expander.

RESULTS

Introduction of 40 Torr of carbon dioxide into a cell containing evaporated manganese produced not only the expected bands

TABLE 1

INFRARED SPECTRA OF SURFACE CO_3 SPECIES FORMED FROM CO_2 AND COMPARISON SPECTRA

CO_3^{2-}	Mn–CO_3	CO_3[a] Bidentate coord.	CO_3[a] Unidentate coord.
ν_3	1580 (C=O str.)	1640–1590	1470–1450
	1305 ($O-\overset{\overset{O}{\|}}{C}-O$ asym. str.)	1290–1260	1370–1360
ν_1	1050 ($O-\overset{\overset{O}{\|}}{C}-O$ sym. str.)	1020–1040	1070–1050
ν_4		710–680	740–780
ν_2	825 (out-of-plane bend)	820–840	850–860

[a] Refs. *3*, *7–9*.

for gaseous carbon dioxide in the 2380 and 716 cm^{-1} regions of the infrared spectrum, but bands were also observed at 1580, 1305, 1050, and 825 cm^{-1}. The latter four bands were assigned to a stable surface compound since several hours of evacuation of the sample produced no detectable decrease in intensity for these bands, whereas the bands in the 2380 and the 716 cm^{-1} regions disappeared after only a short (less than 5 min) evacuation period. The bands due to the surface species that remained after removal of the gaseous and physically adsorbed CO_2 by evacuation of the cell for 30 min are listed in Table 1 and shown as Trace B of Fig. 1.

No infrared bands were found for the interaction of COS or CS_2 with freshly evaporated manganese films. Although no infrared bands were observed for these reactions, volumetric results indicated that carbon disulfide gas was indeed adsorbed on the manganese surface. The addition of successive doses of CS_2 to a bulb containing only a known amount of evaporated manganese metal indicated a rapid uptake of the initial few increments of gas (as noted by the pressure rapidly falling to the point maintained before the gas was added) followed by a slower adsorption of the latter doses until the surface would adsorb no more. After evacuation of the bulb for approximately 15 min, it was again found that the surface would slowly adsorb more CS_2. This process could be repeated several times with similar results; each time the surface slowly adsorbing an amount of CS_2 approximately equal to the amount ad-

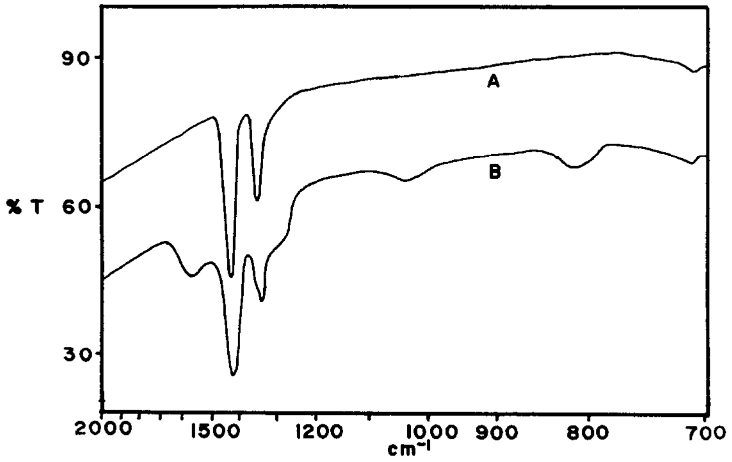


FIG. 1. Carbon dioxide chemisorbed on Mn: Curve A—background; Curve B—surface species after gaseous CO_2 pumped out.

sorbed by the initial slower adsorption process.

Addition of known increments of CO_2 to a bulb containing only fresh evaporated manganese produced a different result. After the addition of each dose of gas, the pressure over the evaporated film fell by only one half the value expected if all of the gas would have been adsorbed by the film. This process continued until the adsorbed material approached complete coverage of the surface at which the pressure in the bulb approached the value expected for no adsorption by the film of that particular dose.

Admission of COS over a freshly evaporated manganese film produced no lowering of the pressure, but results that follow indicate that an interaction did take place.

Introducing 0.5 Torr of either CO_2, COS, or CS_2 into a clean evacuated bulb attached to the quadrupole mass spectrometer produced only the expected peaks for each of the gases, i.e., a parent ion peak plus major fragments such as CO in the case of CO_2 and COS. When 0.5 Torr of each of the above gases was introduced into the bulb containing only evaporated manganese, the results listed in Table 2 were obtained. The results are presented as relative intensities of the major peaks observed both before and after the metal was evaporated. The mass spectra of the gases produced by the interaction of the reactant gases with the manganese evaporated into oil on the windows of the infrared cell and trapped by liquid air agree with those listed above for the metal evaporated into the 250 ml bulb, i.e., before the metal was evaporated the major peak in the spectrum was due to the parent peak of the CO_2 molecule, but after evaporation, the mass spectrum indicated that predominantly CO was present in the cell.

It was determined by infrared spectroscopy that in all cases after the surface had been exposed to either CO_2, COS, or CS_2, it would then not adsorb carbon monoxide. It was also found that CO_2 would readily displace adsorbed carbon monoxide from manganese films and adsorb in its place.

TABLE 2

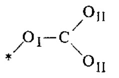
MASS SPECTRAL RESULTS

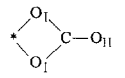
	Relative intensities at masses corresponding to the gases indicated			
Gas added	Clean bulb		Bulb with Mn film	
CO_2	CO	CO_2	CO	CO_2
	.3	1	1	.1
COS	CO	COS	CO	COS
	.7	1	1	.2
CS_2	CS_2		CS_2	
	1		1	

DISCUSSION

Comparison of the infrared spectra obtained in the present study with spectra of the bidentate carbonate formed on Ni (*6*), to the spectra of the general carbonates in coordination chemistry (*1, 8*), and to spectra of unidentate and bidentate carbonate ligands of cobalt compounds (*9*) indicates that the interaction product of carbon dioxide with manganese is a carbonate species. The infrared spectra of known carbonate compounds were not used in this study for comparison purposes to elucidate the specific surface structure. The spectra of such compounds generally show only broad bands not very useful for identification of particular types of bonding of carbonates in coordination chemistry. Also, previous history of the carbonate compounds as well as impurity ions causes variations in the positions of the band centers for the carbonate ions. Many of these problems are reduced to the extent that meaningful assignments can be made when only carbonates are considered which are ligands in coordination compounds (*9*). This approach seems appropriate in that molecules adsorbed at metal surfaces are notably similar to the same molecules contained as ligands in transition metal complexes (*11*). The structure and reactions of coordination complexes have been suggested by a number of authors (*11–15*) as models for catalytic reactions occurring on metal surfaces.

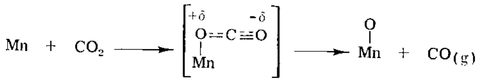
Coordination of the carbonate ion with a metal in the form of a unidentate or a bidentate ligand causes the symmetry to be lowered from D_{3h}, which the free CO_3^{2-} ion possesses, to C_{2v} for both types of coordination. The ν_1 vibration of the carbonate species becomes infrared active due to this lowering of symmetry and both the ν_3 and ν_4 degenerate vibrations split into two components each. Unidentate carbonate complexes with cobalt (*9*) and most other metals (*1*, *8*) show two $C–O_{II}$ stretching bands in the 1470–1450 cm^{-1} and 1370–1360 cm^{-1} regions and one $C–O_I$ stretching band is observed in the 1070–1050 cm^{-1} region. For bidentate carbonate complexes of similar metals, one $C–O_{II}$ stretching band appears in the 1640–1590 cm^{-1} region and two $C–O_I$ stretching bands are observed in the 1290–1260 cm^{-1} and 1040–1020 cm^{-1} regions. Comparison of the frequencies listed in Table 1 indicates that the present results compare well for a bidentate type of adsorption and not so well for a unidentate type.





Since the symmetry is the same for both the unidentate and bidentate species, it was not possible to make a distinction between these two modes of coordination to the surface by means of the selection rules alone. However, it has been pointed out that the splitting of the ν_3 band is much greater in the bidentate than in unidentate coordination (*16*). Taking this into consideration and ruling out an ionic CO_3^{2-} species by an absence of a band corresponding to a ν_4 vibration, the results listed in Table 1 do not seem unreasonable.

The volumetric and mass spectral data can be used to gain insight into a possible reaction mechanism. The results that only half of the carbon dioxide was adsorbed by the surface coupled with the mass spectra data showing the material remaining after the interaction to be predominantly carbon monoxide indicate that two molecules of CO_2 combined on the surface to produce the adsorbed carbonate and release gaseous CO. Since no infrared band for chemisorbed CO was observed it is evident that CO from the dissociation does not chemisorb. Further, the addition of gaseous CO_2 caused the disappearance of infrared bands due to carbon monoxide chemisorbed on a manganese film and the appearance of bands due to the surface carbonate. The overall reaction may be represented by the sequence:

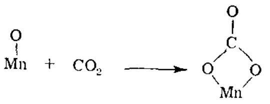


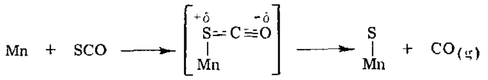
$$Mn + CO_2 \longrightarrow \left[\begin{matrix} \overset{+\delta}{O}{=}C{\equiv}\overset{-\delta}{O} \\ | \\ Mn \end{matrix}\right] \longrightarrow \overset{\overset{O}{|}}{Mn} + CO_{(g)}$$

One molecule of CO is produced for each two molecules of CO_2 consumed in this scheme, accounting for the volumetric results.

Interaction of CO_2 with Ni (*3*, *5*) reported previously and the results of the reaction of CO_2 and manganese found in this study indicate that the two reactions are not entirely similar. While the interaction is dissociative in both cases, carbon monoxide (a product of the reaction) Chemisorbs along with other material on the Ni surface while on Mn the CO does not chemisorb. An explanation for this difference may be found in the different electronic properties of Mn and Ni when the molecular orbital model of chemisorbed CO (*11*) is used. An appreciable amount of π bonding is necessary to stabilize the metal–carbon bond and this π bonding comes from back donation of metal *d* electrons into the metal–carbon–oxygen π molecular orbitals. For zero valent Mn and Ni this readily occurs and chemisorbed CO is stable. However, partial oxidation of the surface during the course of the reaction decreases the availability of metal *d* electrons. For Ni with its almost filled *d* shell, there are still sufficient *d* electrons left after partial oxidation at the surface to stabilize the carbon–metal bond, but for Mn with fewer *d* electrons, there are too few to produce a stable CO surface complex.

Both infrared spectroscopy and volumetric adsorption results gave no indication of interaction between carbonyl sulfide and freshly evaporated manganese. However, mass spectral results, coupled with the fact that the manganese surface was inactivated towards carbon monoxide adsorption after being exposed to COS, indicated that a reaction had occurred. A reaction similar to that for CO_2 and manganese is proposed from the above and from mass spectral results which indicated primarily carbon monoxide gas present after the interaction of COS with the manganese surfaces.





The production of CO from SCO clearly shows that the CS bond is more readily broken that the C–O bond on a manganese surface. The failure of the surface to adsorb CO after exposure to SCO occurs because of the adsorbed sulfur. Infrared absorptions due to metal–sulfur bonds are expected to be beyond the range of our instrument. It is well known that sulfur compounds poison catalytically active surfaces (*17*). If the poisoning is due to sulfiding the surface, the greater ease of breaking C–S bonds than C–O bonds observed here is in line with the experience that carbon–sulfur compounds more readily poison surfaces than carbon–oxygen compounds.

No infrared results were obtained that pointed toward an interaction between CS_2 and evaporated manganese. Also, no evidence of an interaction was found from mass spectral studies. Volumetric results, on the other hand, indicated that CS_2 was taken up rapidly at first followed by a slower additional adsorption which is attributed to weakly held CS_2. After exposure to CS_2 the film would not subsequently adsorb CO.

The results indicate that an interaction between the surface and CS_2 occurred during the initial rapid adsorption and this was a strong interaction since this portion could not be removed by evacuation. This reaction appears to be lesser in extent than the previous two cases.

Garland (*18*) has shown that preadsorbing carbon disulfide on Ni has a poisoning effect on the catalyst, the nature of which is not fully known. An explanation for the Mn system based on the reactions of CO_2 and SCO is that CS_2 dissociates to form manganese sulfide and manganese carbide on the surface. In the cases of carbon dioxide and carbonyl sulfide, dissociation yields the stable gaseous species, carbon monoxide, while in the case of carbon disulfide an analogous stable species does not exist. Therefore, if the reaction proceeds stepwise as in the previous case to break a C–S bond, the remaining C–S fragment would be expected to remain on the surface and dissociate further. If C–S groups had remained intact on the surface in an appreciable concentration, they should have produced observable bands.

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