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Infrared Spectroscopic Investigation of the Adsorption and Reactions of SO_2 on MgO

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SO_2 adsorbs chemically on MgO at room temperature. The adsorbed species transforms to two forms of SO_3^{2-} after heating at 300° under vacuum. Above 500° these sulfite surface species are unstable and either react further or desorb. Only a SO_4^{2-} species remains on the surface. Upon heating in oxygen the SO_3^{2-} species react with O_2 to form bidentate and chelate sulfato complexes along with strongly bonded SO_3.

INTRODUCTION

Mashchenko and coworkers (*1*) and Schoonheydt and Lunsford (*2*) have investigated the adsorption of SO_2 on partially reduced TiO_2 and on activated MgO, respectively, by means of the EPR technique. This technique allowed the investigation of the SO_2^- radical ion only. In both cases the adsorption sites for the SO_2^- are believed to be oxygen ion vacancies. However, SO_2 adsorbs also in a nonparamagnetic form on the surface of these catalysts (*1, 2*). This suggests the existence of other sites on the surface of these catalysts.

It is known (*3–6*) that a suitably pretreated MgO sample contains OH groups, characterized by a typical infrared spectrum. Together with oxygen ion and cation vacancies, they constitute possible adsorption sites for the SO_2 molecules.

On porous silica glass (*7*) SO_2 displaces the 3750 cm^{-1} band of the free hydroxyl groups to a lower wave number by 115 cm^{-1}. On Fe and Ni surfaces SO_2 adsorbs chemically to form a SO_4 surface species, which is believed to be an intermediate in the catalytic oxidation of SO_2 to SO_3 (*8*). Such a strong chemical change is not always observed. Habgood and coworkers (*9*) studied the adsorption of H_2S and SO_2 on γ-alumina, NaOH-doped γ-alumina, NaY and HY zeolites. Except for NaY, where no OH groups were present in measurable amounts, SO_2 adsorbed on these samples through strong hydrogen bonding. After heating up to 400° under dynamic vacuum the adsorbed SO_2 molecules on γ-alumina and on NaOH-doped γ-alumina transformed to a chemisorbed species. A sulfate-like structure involving two lattice oxygens and the adsorbed SO_2 molecule was suggested as an explanation. However, the Si–O and Al–O adsorption bands in the 700–1200 cm^{-1} region obscure the S–O vibrations of this SO_4 species and no unambiguous proof could be advanced by these authors (*9*).

The infrared spectrum of SO_2 on CaO has recently been studied by Low and coworkers (*10*). They observed that the main interaction of SO_2 with degassed CaO is irreversible and leads to the formation of a surface sulfite; however, reversible chemisorption occurs at high degrees of surface coverage. On heating the sample under vacuum at 550° a new spectrum attributed to a surface sulfate was observed.

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At higher temperature further conversion to the sulfate and polymerization are thought to occur. Heating in oxygen resulted in a spectrum which resembles that of bulk $CaSO_4$.

These data suggest that both physisorption and chemisorption could occur upon sorption of SO_2 on MgO. Chemisorption could occur through reaction with surface oxide ions to form compounds of the type $S_xO_y^{2-}$. Both processes can be investigated with the infrared technique. Physisorption on OH groups results in a shift of the OH stretching frequency of MgO toward lower wave numbers. The many possible types of $S_xO_y^{2-}$ ions can be identified by their characteristic S–O frequencies in the infrared spectrum.

EXPERIMENTAL

Reagent grade, powdered MgO was supplied by Mallinckrodt Chemical Works. The powder was boiled in distilled water for 2–3 hr and allowed to settle on the bottom of a container under a water layer. A small amount of MgO paste was spread out over a 2 × 1 cm platinum grid. The film obtained in this way was fitted in the quartz side-arm of the infrared cell depicted in Fig. 1. One sample was studied without the platinum grid in order to demonstrate that the platinum did not influence the reactions. Because of the platinum grid it is difficult to give an accurate sample density; however, a value of 20 mg/cm^2 of MgO may be used for comparison purposes.

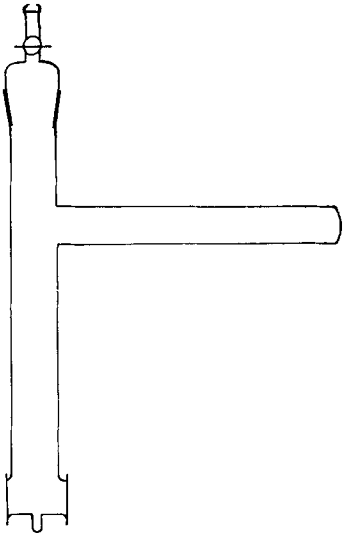


FIG. 1. Infrared cell with quartz side-arm and AgCl windows.

Typical pretreatments consisted in evacuating the sample in the side-arm of the cell to 1×10^{-5} Torr and subsequently heating it up to 300, 500 and 800° for 3–7 hrs. After cooling the film was allowed to glide between the two AgCl windows. Magnesium oxide is not transparent below 700 cm^{-1}. Spectra were taken at room temperature under vacuum, in the regions 700–1700 cm^{-1} and 3100–3800 cm^{-1} after each pretreatment. About 3 Torr of pure SO_2 was allowed into the cell. Spectra were taken in the same wave number regions directly after the SO_2 introduction and at several stages of the subsequent desorption-reaction process. In this latter procedure the sample was heated under vacuum up to 800° in intervals of 200°. The sample was equilibrated for 2 hr at each 200° interval, cooled, and the spectrum was taken at room temperature.

The reactivity of the adsorbed species towards O_2 was also investigated. For this purpose SO_2 was adsorbed and subsequently degassed at 500° for 2 hr under vacuum. The spectrum was taken from 700–1500 cm^{-1} and 3100–3800 cm^{-1} at room temperature. This was followed by the introduction of about 150 Torr O_2.

The sample was then heated for 2 hr in the O_2 atmosphere at 200, 400, 600 and 800°, respectively. After each step the spectra were recorded in the same wave number ranges at room temperature without previous evacuation of the excess O_2.

Finally, for the purpose of comparison, spectra were obtained at room temperature from MgO doped with $MgSO_4$ and $MgSO_3$ solutions after degassing at 500° under vacuum.

All infrared spectra were recorded with a Beckman IR-12 spectrophotometer in the absorbance mode. The estimated error in the assignment of wave numbers is ±5 cm^{-1} for sharp bands and ±10 cm^{-1} for broad bands.

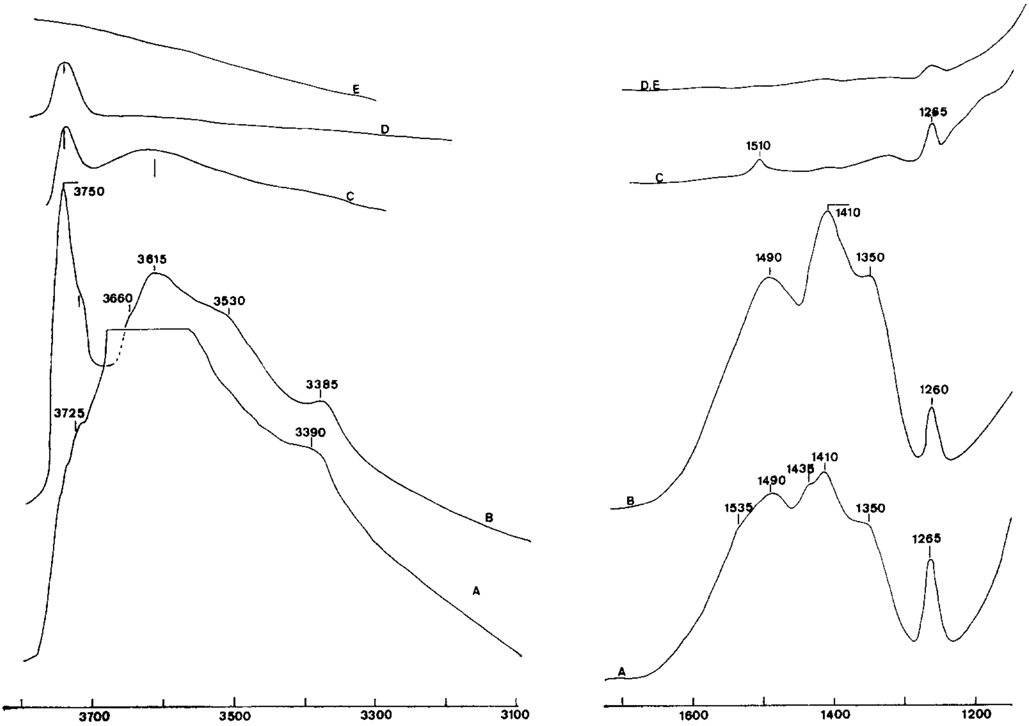


FIG. 2. The infrared spectra of MgO at several dehydration temperatures: A. after 2 hr heating at 250°; B. after 2 hr heating at 300°; C. after 2 hr heating at 400°; D. after 2 hr heating at 500°; E. after 2 hr heating at 800°.

RESULTS

The ir Spectrum of MgO Following Pretreatment at 250–800°

Spectra of MgO at several stages of dehydration were recorded in the regions 1100–1700 cm^{-1} and 3000–3800 cm^{-1}. They are displayed in Fig. 2. Heating the sample for 2 hr at 250° resulted in a huge band in the region 3600–3670 cm^{-1} with a shoulder at 3390 cm^{-1} (Fig. 2A). In the 1100–1700 cm^{-1} region bands were observed at 1265, 1350, 1410, 1435, 1490 and 1535 cm^{-1}. Following dehydration at 300° the 1535 and 1435 cm^{-1} bands disappeared (Fig. 2B). In the OH stretching region the most intense band appeared at 3750 cm^{-1} with a shoulder at 3725 cm^{-1}. The band in the 3600–3670 cm^{-1} region was strongly reduced in intensity and three components at 3660, 3615 and 3530 cm^{-1} may be resolved. The 3390 cm^{-1} band remained unchanged.

At dehydration temperatures above 300° all these bands decreased rapidly in intensity. At 400° only bands at 1265 and 1500 cm^{-1} remained in the 1100–1700 cm^{-1} region (Fig. 2C). Bands occurred also at 3750 cm^{-1} and 3615 cm^{-1}, although strongly reduced in intensity. At 500°, only the 3750 cm^{-1} band was visible in the spectrum (Fig. 2D), and at 800° no infrared bands were observed in the regions investigated (Fig. 2E). Table 1A summarizes the OH bands observed in the 3000–3800 cm^{-1} region.

The ir Spectrum of SO_2 Adsorbed on MgO at Room Temperature

Beside the bands due to gaseous SO_2 at 1340 and 1150 cm^{-1}, a broad band was observed between 800 and 1100 cm^{-1} after adsorption of SO_2. The 3750 cm^{-1} band disappeared but a new broad band developed around 3655 cm^{-1}. The 3725–3730 cm^{-1} shoulder remained unaltered. Bands were always present at 3575 and around 3450 cm^{-1} but were not always clearly

TABLE 1

FREQUENCIES OF THE OBSERVED ir BANDS AND THEIR ASSIGNMENT

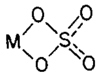
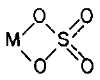
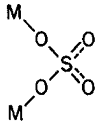
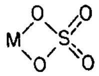
A. *OH band spectrum of MgO*

Pretreatment temperature °C	Frequency (cm^{-1})	Assignment
300	3750	free, accessible OH
	3725	partially inaccessible OH
	3615	Hydrogen bonded OH
	3660	OH group in Mg(OH)$_2$
	3530	OH group in Mg(OH)$_2$
	3390	OH group in Mg(OH)$_2$

B. *Bands formed during desorption of SO$_2$ under vacuum*

Degassing temperature °C	Frequency (cm^{-1})	Assignment
300–500	895	SO$_3^{2-}$ (A)
	925	SO$_3^{2-}$ (A)
	975	SO$_3^{2-}$ (A), SO$_3^{2-}$ (B)
	1040	SO$_3^{2-}$ (B)
	1070	SO$_3^{2-}$ (B)
	955	?
800	860	SO$_4^{2-}$
	1020	SO$_4^{2-}$
	1070	SO$_4^{2-}$

C. *Bands formed during reaction of adsorbed SO$_2$ with O$_2$*

Reaction temperature °C	Frequency (cm^{-1})		Assignment
400	3740–3750		free OH
	3640		Mg–OH SO$_3$
	3430		Mg–OH SO$_3$
	1345 1060		SO$_3$
	1240 1120 1060 980		 (1)
	1290 1175 1015 910		 (2)
	1195 1120 1045 980		
800	1390 1360 1050	SO$_3$	 (3)
	1220 1170 1050 950		

resolved because of their broadness. These features were independent of the pretreatment temperature, except for the 800° pretreatment where no detectable amounts of OH groups were left on the MgO surface. Figure 3A gives an example of the spectra obtained following removal of SO$_2$ by evacuating at room temperature for 20 min. The MgO sample had been pretreated at 500°.

The Desorption and Reaction of SO$_2$ at Elevated Temperatures

Figures 3B–E give typical spectra from the desorption and reaction of SO$_2$ with the surface upon heating the sample to increasingly higher temperatures under dynamic vacuum. After heating 1.5 hr at 220° under vacuum no changes occurred in the 800–1100 cm^{-1} region. The bands in the OH stretching region were better resolved and occurred at 3400, 3600, 3670 and 3730 cm^{-1} (Fig. 3B). The latter was increased somewhat in intensity. Further heating for 2 hr at 420° restored the 3740–3750 cm^{-1} band, while the other bands in the OH region disappeared (Fig. 3C). The 800–1100 cm^{-1} region was completely altered. Five intense bands were resolved: two partially overlapping bands at 895 and 925 cm^{-1}, a band at 975 cm^{-1} and a band at 1040 cm^{-1} with a shoulder at 1070 cm^{-1}

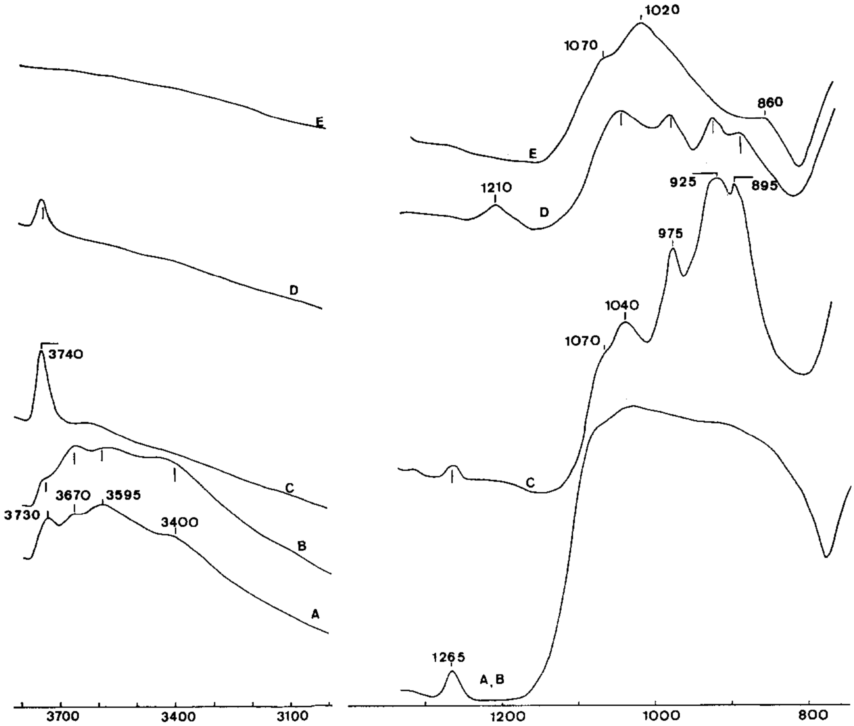


FIG. 3. The infrared spectra of SO_2 and its reaction products adsorbed on MgO after degassing *in vacuo* (MgO pretreated at 500°): A. at room temperature for 20 min; B. at 220° for 1.5 hr; C. at 420° for 2 hr; D. at 600° for 2 hr; E. at 800° for 2 hr.

Up to 500° this five-band spectrum was unaltered.

Above 500° all the bands decreased strongly in intensity as seen in Fig. 3D. At 800° no OH bands were left in the 3300–3800 cm^{-1} region and three broad bands at 860, 1020, and 1070 cm^{-1} remained in the 800–1100 cm^{-1} region, regardless of the pretreatment of the MgO sample. A summary of the bands observed under various conditions and their assignments, as explained in the discussion, are given in Table 1B.

A sample pretreated at 330° behaved essentially in the same manner. Its OH bands at 3750 and 3615 cm^{-1} were shifted to lower frequencies at 3655, 3590 and 3400 cm^{-1}. Desorption of SO_2 at 300° for 2 hr restored the two original OH bands. At the same time the five-band spectrum appeared in the 800–1100 cm^{-1} region with an additional weak band at 955 cm^{-1}. The latter disappeared after degassing at 500°.

For MgO pretreated at 800° the same five-band spectrum occurred in the 800–1100 cm^{-1} region at only 300°, although strongly reduced in intensity with respect to the samples pretreated at 330 and 500°. This reduction in intensity is probably due to a loss in surface area. Some overlapping occurred with the bands at 1020, 1070 and 860 cm^{-1}. As a consequence, the band at 1040 cm^{-1} was not resolved. The bands at 1070 and 1020 cm^{-1} appeared more intense than the bands at 975, 925 and 895 cm^{-1}. This is the reverse of the behavior observed for the samples pretreated at 330 and 500°. The infrared spectrum of SO_2 adsorbed and reacted even at 300° on MgO pretreated at 800° has the characteristic features of SO_2 reacted at 800° on MgO pretreated at 500°.

The Reactivity of Adsorbed SO_2 with O_2

After desorption of SO_2 under vacuum at 500° the residual adsorbed SO_2 species were allowed to react with O_2 at 200° and at increasingly higher temperatures up to

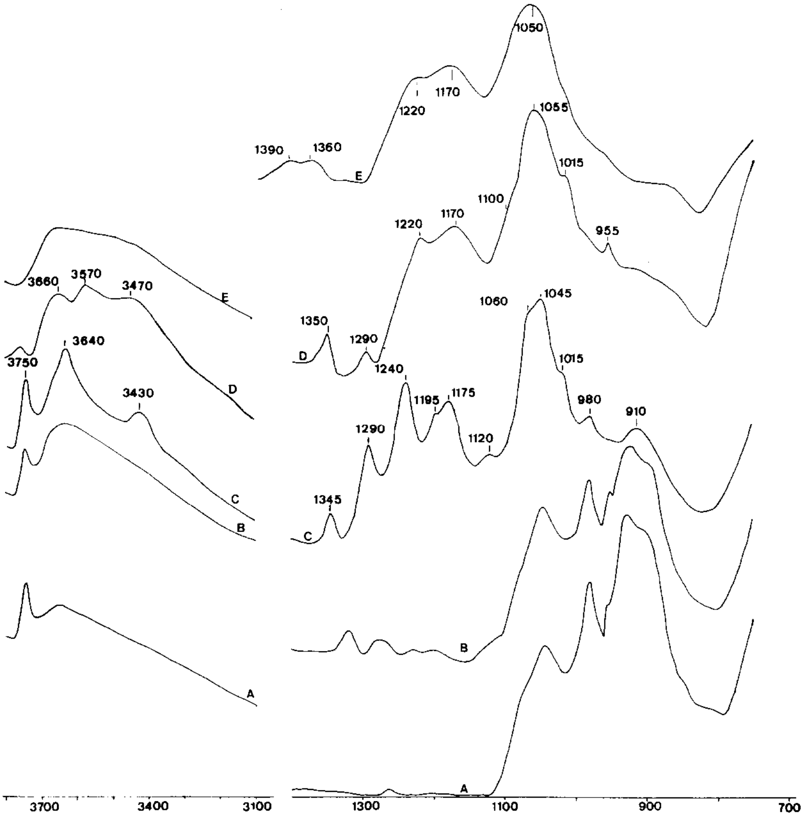


FIG. 4. The infrared spectra of sulfite species on MgO before and after reaction with O_2: A. sulfite on MgO after 2 hr degassing at 500° *in vacuo;* B. heating 2 hr in excess O_2 at 200°; C. after 2 hr in excess O_2 at 400°; D. after 2 hr in excess O_2 at 600°; E. after 2 hr in excess O_2 at 800°.

800°. The equilibration time at each temperature was 2 hr. Figure 4 displays the spectra obtained for MgO pretreated at 500°.

Very little change was observed in the spectra after 2 hr heating at 200°, except for the fact that in the 1100–1400 cm^{-1} region (Fig. 4B) bands began to appear at the expense of the bands in the 800–1100 cm^{-1} region. This was clearly evident after the 400° treatment: new bands occurred at 1345, 1290, 1240, 1195, 1175 and 1120 cm^{-1} (Fig. 4C). Weak bands appeared at 910 and 980 cm^{-1} while the 1040 cm^{-1} band with its shoulder at 1070 cm^{-1} was replaced by a triplet at 1015, 1045 and 1060 cm^{-1}. Drastic changes occurred also in the OH stretching region where two new bands appeared at 3640 and 3430 cm^{-1} besides the 3750 cm^{-1} band.

Upon reaction at 600° the bands in the 3100–3800 cm^{-1} region decreased in intensity and became broader (Fig. 4D). The 3640 and 3430 cm^{-1} bands were shifted to 3650 and 3470 cm^{-1}, respectively. A new band was evident at 3570 cm^{-1}. The 800–1500 cm^{-1} region was completely changed. The 1290 cm^{-1} band was reduced in intensity, and the four bands in the 1100–1250 cm^{-1} region, originally present after heating at 400°, were replaced by two strong bands at 1220 and 1170 cm^{-1}. The triplet around 1050 cm^{-1} occurred at 1015, 1055 and 1100 cm^{-1}. A weak band at 955 cm^{-1} was the only one remaining at the lower wave numbers.

After 2 hr in oxygen at 800° the OH band spectrum disappeared completely. A broad band was observed around 1050 cm^{-1} (Fig. 4E). It is probably composed of three components, equivalent to the triplet described above. Also, the 1220 and 1170

cm^{-1} bands became broader. Two new weak broad bands appeared around 1360 and 1390 cm^{-1}. Table 1C summarizes the observed frequencies and their assignment as explained in the discussion section.

In order to obtain bands with detectable intensity for MgO pretreated at 800°, the SO_2 was not degassed at 500° under dynamic vacuum prior to heating in excess O_2. No bands were observed in the 3100–3800 cm^{-1} region. After heating 2 hr at 400° in excess O_2 a spectrum was obtained similar to that shown in Fig. 4E with the exception of the 1360 and 1390 cm^{-1} bands. Also the band envelopes at 1220 cm^{-1} and 1170 cm^{-1} were more intense than the band envelope at 1050 cm^{-1}. For MgO pretreated at 500° the reverse intensity ratio was observed.

The ir Spectra of $MgSO_3$ and $MgSO_4$ on MgO

By way of comparison Fig. 5 shows the spectra of MgO doped with solutions of $MgSO_3$ and $MgSO_4$ and subsequently degassed at 500°. The $MgSO_3$ spectrum was not well resolved; however, it resembles qualitatively the spectrum obtained by heating SO_2 on MgO under vacuum at 500°. A broad adsorption occurred in the region 890–925 cm^{-1} together with bands at 980 cm^{-1} and at 1040 cm^{-1}. The latter had a shoulder at 1080 cm^{-1}. In addition three bands occurred around 1180, 1220 and 1265 cm^{-1}.

$MgSO_4$ gave a better resolved spectrum. A triplet was observed at 1055, 1040 and 1015 cm^{-1}. Two weak bands were observed at 950 and 980 cm^{-1}. Bands of medium intensity occurred at 1338, 1260, 1215 and 1195 cm^{-1}. A shoulder was observed at 1215 cm^{-1}.

DISCUSSION

The Hydroxyl Band Spectrum of MgO

Imelik and coworkers (*4*) reported that physisorbed water was desorbed from MgO at 150° under dynamic vacuum. This treatment also eliminated the 1640 cm^{-1} deformation band of water. Therefore, the bands in the 1100–1700 cm^{-1} region reported in Fig. 2 can not be ascribed to water. We rather believe that they are due to carbonate species on the surface. The frequencies fall in the same range as those reported in the literature for carbonate species (*11*).

Anderson (*3*) observed bands at 3750, 3710 and 3620 cm^{-1} which are ascribed to three types of OH groups on the MgO surface. The 3750 cm^{-1} band is attributed to isolated OH groups pointing out of the surface; whereas, the 3620 cm^{-1} band is assigned to OH groups with their oxygens linked to two Mg ions. The band at 3710 cm^{-1} only appeared after rehydration of MgO and is ascribed to an intermediate product between MgO and $Mg(OH)_2$. Lisachenko *et al.* (*6*) disagree with this interpretation of the 3620 and 3710 cm^{-1} bands. They interpret the 3620 cm^{-1} band

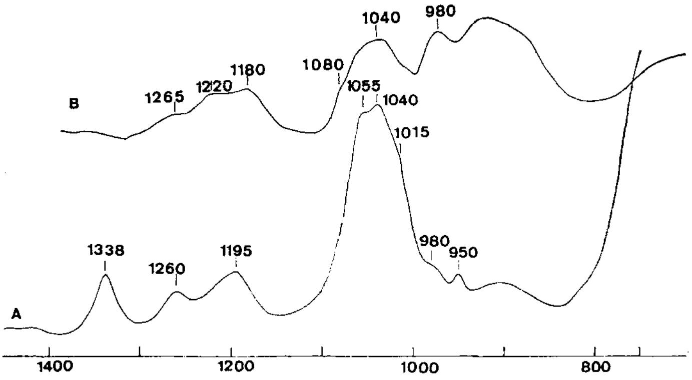
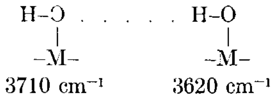


FIG. 5. A. Infrared spectrum of MgO doped with a $MgSO_4$ solution and subsequently degassed at 500° for 2 hr. B. Infrared spectrum of MgO doped with a $MgSO_3$ solution and subsequently degassed at 500° for 2 hr.

as due to hydrogen bonded hydroxyl groups and the 3710 cm^{-1} band as due to hydroxyl groups with a free proton but with their oxygen hydrogen bonded to a neighboring OH group:



$$\begin{array}{ccc} \text{H–O} & \cdots\cdots & \text{H–O} \\ | & & | \\ \text{–M–} & & \text{–M–} \\ 3710\ cm^{-1} & & 3620\ cm^{-1} \end{array}$$

After heating at 300° we reported three additional bands at 3660, 3530 and 3390 cm^{-1}. These may be ascribed to preferred geometric arrangements for other hydrogen bonded OH groups. We agree with previous investigators (*3–6*) concerning the assignment of the 3750 cm^{-1} band to isolated hydroxyl groups. However, as indicated in Fig. 2, the 3710 cm^{-1} band, which occurs at 3725 cm^{-1} in our case, is already present during the initial dehydration process in contradiction with Anderson's work (*3*). Moreover, our adsorption data with SO_2 revealed that a similar band (3730 cm^{-1}) is present after adsorption. This suggests that the band is due to OH groups in the bulk MgO or that they are screened off from the SO_2 molecules by inaccessible pores.

From our data it is impossible to decide whether Anderson's interpretation (*3*) or Lisachenko's (*6*) is correct concerning the 3620 cm^{-1} OH groups. The broadness of the bands and the fact that these OH groups are more easily dehydrated than the 3750 cm^{-1} OH groups are experimental results in favor of Lisachenko's interpretation.

The Species Formed during the Adsorption and Desorption of SO_2 under Vacuum

No SO_2 bands around 1360 cm^{-1} and 1150 cm^{-1} are left in the spectrum after degassing the excess SO_2 at room temperature; hence, no physisorbed SO_2 remains on the surface. At the same time the 3740–3750 cm^{-1} OH band does not reappear. To restore this 3750 cm^{-1} band it is necessary to heat the sample to 300°.

The complex OH band spectrum of Fig. 3A and B contains the 3725–3730 cm^{-1} band, attributed to inaccessible OH groups, and three bands around 3670, 3600 and 3400 cm^{-1}. The latter can only come from the original 3750 cm^{-1} band. The shifts to three lower frequencies could indicate three different strengths of interaction with only one sulfur species adsorbed on three different sites. It is, however, more probable that three different sulfur species are present on the surface. Each of them interacts with OH groups. This results in three different frequency shifts according to the type and strength of interaction in each individual case.

The broad band between 800–1100 cm^{-1} (Fig. 3A and B) does not allow an identification of the possible sulfur species on the surface at low temperatures. It is possible that SO_2 is present in the form of a strongly complexed surface species. In sulfinato complexes, where SO_2 is linked with one oxygen or both oxygens to the complexing ion, the free S–O stretching vibration absorbs in the range 1100–1050 cm^{-1} while the ν_{as} (S–O–M) vibration absorbs at still lower wave numbers. The difference between the two frequencies is 100–200 cm^{-1} for sulfinato, O-complexes and 10–80 cm^{-1} for sulfinato O, O′-complexes (*12*). These frequencies fall in the broad absorption range of 800–1100 cm^{-1}, but the existence of such complexed SO_2 cannot be verified from our experiments.

At 300° the 3750 cm^{-1} band is completely restored, which indicates that no OH groups remain hydrogen bonded or react with the sulfur species. At the same time the broad 800–1100 cm^{-1} absorption goes over to the five-band spectrum shown in Fig. 3C. The most reasonable explanation is that certain surface species of SO_2 are desorbed and others react with the MgO surface.

The spectrum of Fig. 3C agrees qualitatively with that of MgO doped with $MgSO_3$ (Fig. 5B). In the latter spectrum bands occur also at 1220 and 1265 cm^{-1} which are not present in the degassed MgO samples of Fig. 3C. The origin of these bands is not known. In the 800–1100 cm^{-1} region the free SO_3^{2-} has a nondegenerate vibration ν_1 at 961 cm^{-1} and a doubly degenerate vibration ν_3 at 1010 cm^{-1} (*13*). If the C_{3v} symmetry is lowered to C_s the 1010 cm^{-1} band splits into two bands. Splitting of the degenerate ν_3 vibration of SO_3 occurs in sulfito complexes (*14*, *15*). If the SO_3^{2-} ion is bonded with its S atom to the surface the C_{3v} symmetry is preserved. If bonding occurs through O the symmetry can be lowered to C_s for unidentate complexes while it is always C_s in bidentate complexes. Furthermore, coordination through sulfur shifts the SO stretching bands to higher frequencies, whereas coordination through oxygen shifts them to lower frequencies relative to the frequencies of the free ion (*13*).

In sulfito bidentate complexes Baldwin (*14*) observed the ν_1 at 988 cm^{-1} and the two bands of ν_3 in the regions 1093–1070 cm^{-1} and 1036–1042 cm^{-1}. These frequencies agree reasonably well with the 975 cm^{-1}, 1040 and 1070 cm^{-1} bands observed in our spectra (Fig. 3C). This observation together with the similarity to the spectrum of $MgSO_3$ doped MgO is strong evidence for the existence of a SO_3^{2-} surface species on MgO. We believe also that the pair of bands at 925 cm^{-1} and 895 cm^{-1} belongs to the nearly degenerate ν_3 (*E*) vibration of a second SO_3^{2-} species. The latter species is less stable than the former as can be seen from Fig. 3D. Following this reasoning the 1040–1070 cm^{-1} pair of bands is assigned to a SO_3^{2-} species coordinated through its sulfur while the 925–895 cm^{-1} pair of bands is assigned to a SO_3^{2-} species coordinated through an oxygen atom.

Also some samples have a weak 955 cm^{-1} band which completely disappears at 500°. The origin of this unstable band is unknown.

The 800° pretreated MgO has only weak SO_3^{2-} bands at the same frequencies as those shown in Fig. 3C. This indicates the presence of very small amounts of SO_3^{2-}. One reason for this decrease is the loss in surface area due to the 800° pretreatment with respect to the 500° pretreatment. It also appears that the SO_3^{2-} may react to form other species since sulfite salts are unstable above 500°. The spectra of the SO_2 adsorbed on MgO pretreated at 800° predominantly show the features of the spectrum of SO_2 on MgO pretreated at 500° and subsequently degassed at 800°, i.e., two broad bands at 1070 and 1020 cm^{-1} with a peak around 860 cm^{-1}. The most reasonable explanation for these bands is the formation of some SO_4 species. Blyholder and Cagle (*8*) also give three frequencies at 865, 955 and 1055 cm^{-1} for a surface SO_4 species on Fe. Our frequencies on MgO fall in approximately the same range. A comparison of these frequencies with those of sulfato complexes indicates that a monodentate complex is probably formed on the surface (*13*).

A comparison of the spectra of SO_2 adsorbed on MgO and CaO reveals significant differences, although the overall reactions are similar. At low coverages it appears that SO_2 reacts with CaO at 25° to form a pyramidal sulfite (*10*). This assignment by Low and coworkers is based on the observation of bands at 973, 925, and 632 cm^{-1}. The bands at 973 and 927 cm^{-1} are in agreement with two of those observed for SO_3^{2-} (*A*) on MgO. The rather complex spectrum obtained by degassing the CaO–SO_2 sample to 500° has been attributed to a surface sulfate; whereas, we attribute a somewhat similar spectrum to the formation of two sulfite species. Following treatment of the samples at 750–800° a much more complex spectrum was observed on CaO than on MgO. The resulting spectra were assigned to species such as $S_2O_3^{2-}$, $S_2O_5^{2-}$, $S_3O_8^{2-}$, etc., for CaO and SO_4^{2-} for MgO.

Reaction of Adsorbed SO_2 with O_2

It is apparent from the spectra of Fig. 4 that the sulfito groups on MgO react with oxygen to form new surface species. At least eleven bands are apparent in the spectrum of Fig. 4C and other weak bands may be hidden beneath the dominant ones. As the temperature is raised to 600 and 800° some of the bands diminish while new bands appear. Although the situation is complex, one may make reasonable assignments concerning the origin of the bands.

The oxidation products are probably

sulfato complexes. The free sulfate ion has T_d symmetry. Its ν_3 and ν_4 vibrations are infrared active at 1105 and 613 cm^{-1}, respectively (*13*). When the ion is bonded through one oxygen the forbidden ν_1 vibration is allowed at 970 cm^{-1} and the triply degenerate ν_3 vibration splits into two bands. For a bidentate complex where SO_4^{2-} is bonded with two oxygens, the symmetry becomes C_{2v} with three bands from the split ν_3 vibration in addition to the one band from the ν_1 vibration. Two types of bidentate complexes are possible; one is a chelating complex and the other is a bridging complex. Typically the ν_3 vibrational frequencies of the chelating complex (1230, 1120, 1060, and 960 cm^{-1}) are higher than those of the bridging complex (1160, 1100, 1030, and 970 cm^{-1}) (*13*).

As indicated in Table 1C, the bands observed following reaction of the sulfito complex with oxygen at 400, 600 and 800° may be divided into three chelating and one bridging complex. Since the thermal treatment at 800° produces a drastic modification of the surface, it is not surprising that the surface complexes are different at 800° compared to 400°. A bridging complex and a sulfato complex denoted by C_1 were the first to decrease and a new complex appeared following reaction at 600°. The spectrum of a second chelating complex, C_2, was also weaker at this temperature. Such concomitant behavior of certain bands was used to make the assignments. At 600° a new chelating complex, C_3, appeared which was the dominant species following reaction at 800°.

At all three reaction temperatures bands appeared in the 1345–1390 cm^{-1} region with a possible counterpart in the 1050–1060 cm^{-1} region. Free SO_3 exhibits bands at 1391 and 1068 cm^{-1}; hence, it is reasonable to assume that the similar bands on MgO are due to strongly adsorbed SO_3 which is in equilibrium with the sulfato complexes. The hydroxyl bands at 3640 and 3430 cm^{-1} may be shifted and the OH^- groups stabilized by interactions with the strongly bonded SO_3. The assignment of the bands to SO_3 is supported by the observation that the 1360 and 1390 cm^{-1} bands did not appear on MgO pretreated at 800°, and the counterpart of the SO_3 spectrum at 1050 cm^{-1} became less important than the pair of bands at 1170 and 1220 cm^{-1}. Pretreatment at 800° must destroy the sites responsible for the formation of the SO_3 species.

Low and coworkers (*10*) likewise studied the reaction of adsorbed sulfur species with oxygen at elevated temperatures. They observed that the sulfate band pattern produced by degassing the sample at 750° became more like that of an ionic sulfate upon reaction with oxygen. They concluded that small patches or microcrystals of $CaSO_4$ are formed on the CaO surface. The spectrum of Fig. 5C is probably due, in part, to the formation of corresponding microcrystals on MgO. A comparison of this spectrum with those of Fig. 4C–E shows that similarities exist; however, the presence of distinctly different bands indicates that more than one type of sulfate species is formed upon reaction with oxygen.

CONCLUSIONS

At room temperature SO_2 chemisorbs on the surface of MgO. From the broad absorption in the 800–1100 cm^{-1} region no assignment to a specific sulfur species can be made. Heating under vacuum results in some desorption and, at the same time, two different SO_3^{2-} species became apparent on the surface. These two species correspond to two different active sites on the surface of MgO. The number of sites, as reflected by the intensity ratio of the bands of the two SO_3^{2-} species, depends on the pretreatment of the MgO catalyst. At temperatures above 500° SO_3^{2-} is unstable and decomposes. As a consequence, after degassing at 800° under vacuum residual bands are present which are attributed to a SO_4^{2-} surface species.

When the SO_3^{2-} ion is heated in O_2, a complex infrared spectrum is observed at 400°. It corresponds to a mixture of bidentate and chelate sulfato complexes along with strongly bonded SO_3. At higher temperatures only one sulfato group and the SO_3 remain on the surface.

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