# General and Inorganic Chemistry

## Chemisorption of $SO_2$ and $Cl_2$ on indium oxide

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The mutual influence of $SO_2$ and $Cl_2$ during their consecutive chemisorption on the $In_2O_3$ surface has been investigated. It was found that $SO_2$ is chemisorbed in the uncharged form, and the amount of chemisorption decreases as the temperature increases. The preliminary chemisorption of $Cl_2$ results in a dramatic decrease in the amount of $SO_2$ sorbed and in a change in the character of the bonding of $SO_2$ with the oxide surface. When $SO_2$ is sorbed first, the temperature of the formation of chlorides during subsequent chemisorption of $Cl_2$ decreases.

**Key words:** chemisorption, surface, active sites, electric conductivity.

The studies on the chemisorption of $SO_2$ and $Cl_2$ on ZnO carried out previously[1] showed that the character of the interaction of these gases with the surface of semiconducting oxides depends on the order in which they are adsorbed. In the present work we have studied the mutual influence of $SO_2$ and $Cl_2$ during their consecutive sorption on the surface of $In_2O_3$.

### Experimental

Investigations were carried out at 23—225 °C, the pressure of the gas being sorbed was 0.1—0.5 Torr, and the unit that was used allowed the variation of the pressure and of the electrical conductivity of the sample to be simultaneously recorded.[1] The electrical conductivity varied in the range $10^{-7}$—$10^{3}$ Ohm $cm^{-1}$.

An $In_2O_3$ specimen of the "pure" grade with $S_{spec}$ = 6.0 $m^2$ $g^{-1}$ was used. Its electrical conductivity in air was 0.1 Ohm $cm^{-1}$. Prior to the experiment, the sample was placed into a measuring cell and aged for 16—20 h at 350 °C until constant electrical conductivity (1.0—5.0 Ohm $cm^{-1}$) was attained, then the cell was filled with the gas to be sorbed. When the chemisorption was completed, the amount of reversibly sorbed gas was determined by freezing it out in a trap cooled with liquid nitrogen. Chemisorption was regarded as irreversible if no desorption from the surface occurred at the experimental temperature in the course of 2 h.

After the study of the interference of $SO_2$ and $Cl_2$ under the conditions of their consecutive chemisorption, the sample was evacuated for 2 h at the experimental temperature, and the second gas was introduced.

The composition of the products of the interaction was determined by the thermodesorption method using an MI-1201 mass spectrometer.[2]

### Results and Discussion

The sorption of $Cl_2$ on the $In_2O_3$ surface (see Ref. 3) occurs irreversibly, increases with increasing tempera-

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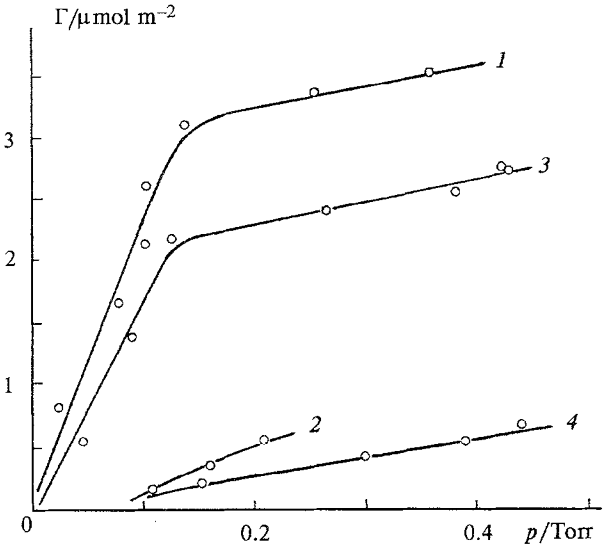

**Fig. 1.** Isotherms of the chemisorption of $SO_2$ on $In_2O_3$ at 23 °C (*1, 2*) and 200 °C (*3, 4*); *1, 3* are the irreversible form and *2, 4* are the reversible form.

ture, and is accompanied by a decrease in the electrical conductivity of the oxide due to localization of the conduction electrons on the sorbed particles.

The chemisorption of $SO_2$ occurs at a high rate; the kinetics of the chemisorption is described by the Zel'dovich—Roginskii equation:[4]

$$\Gamma = a \log \tau + b$$

Two forms of the adsorption of $SO_2$ were found in the temperature range studied, *i.e.*, reversible and irreversible adsorption. 90 % of the gas is sorbed reversibly. Figure 1 shows the isotherms of $SO_2$ adsorption. The isotherms of irreversible sorption are curves that have long initial linear sections (up to a filling degree of 47 % of the monolayer at 23 °C and up to 30 % at 200 °C) and are typical of a surface that is uniform with respect to the heat of sorption.

The amounts of both reversible and irreversible sorption decrease as the temperature increases. In fact, at 23 °C, reversibly sorbed gas occupies 6.5 % of the monolayer (this evaluation is based on the geometric size of the molecule and the assumption that the surface has a continuous coating), while irreversibly sorbed gas covers 50.1 %. As the temperature increases to 200 °C, filling of the surface with the irreversibly sorbed gas decreases to 43.3 % of the monolayer, and filling with the reversibly adsorbed gas decreases to 5.6 %. Thus, the proportion of the reversible form is identical in both cases and is 11.5 % of the total amount of the gas sorbed.

The chemisorption of $SO_2$, in contrast to that of $Cl_2$, is not accompanied by variation of the relative electrical conductivity ($\sigma/\sigma_0$). The $\sigma/\sigma_0$ value does not exceed 5.5 % over the whole temperature range studied, *i.e.*, $SO_2$ is predominantly chemisorbed on $In_2O_3$ in a weak uncharged form. Reversible and irreversible sorption are likely to occur on active sites of the same nature. In fact, according to the data of mass spectroscopic analysis, $SO_2$ is removed from the surface in the unchanged form; $SO_2$ sorbed at 23 °C is removed at 190 °C, and that sorbed at 200 °C is eliminated at 310 °C.

A comparison of the quantities of $Cl_2$ and $SO_2$ sorbed showed that under identical conditions ($T$ and $p_0$) filling of the surface with $SO_2$ is twice as high as that with $Cl_2$ (Table 1). In the case of the consecutive sorption of $Cl_2$ and $SO_2$, the situation changes dramatically. Preliminary chemisorption of $Cl_2$ results in a substantial (an order of magnitude) decrease in the amount of $SO_2$ sorbed. The results obtained make it possible to infer that the sorption of both $Cl_2$ and $SO_2$ occurs on sites of the same type. Since metal atoms[5] are known to be the sites where the chemisorption of $Cl_2$ with charge transfer occurs, in the absence of $Cl_2$, the molecules of $SO_2$ must also occupy the same sites.

**Table 1.** Chemisorption of $Cl_2$ and $SO_2$ on the surface of $In_2O_3$ (the initial pressure of the gas being sorbed was 0.5 Torr)

| Gas | $T$/°C | Coefficients of Eq. (1) | | Filling of the surface | | The relative variation in the electrical conductivity, $\sigma/\sigma_0$ |
|---|---|---|---|---|---|---|
| | | $a$ | $b$ | μmol m$^{-2}$ | % of the monolayer | |
| $Cl_2$ | 23 | 0.064 | 0.363 | 0.66 | 10.0 | 0.444 |
| | 100 | 0.134 | 0.321 | 0.74 | 11.2 | 0.110 |
| | 150 | 0.158 | 0.327 | 0.93 | 14.1 | 0.086 |
| | 200 | 0.206 | 0.644 | 0.98 | 14.8 | 0.665 |
| $SO_2$ | 100 | 3.204 | −3.992 | 1.44 | 21.2 | 0.980 |
| | 150 | 2.355 | −2.892 | 1.17 | 17.7 | 1.050 |
| | 225 | 2.152 | −4.422 | 0.94 | 14.2 | 1.010 |
| $SO_2$ after $Cl_2$ | 100 | — | — | 0.09 | 1.4 | 1.270 |
| | 150 | — | — | 0.28 | 4.2 | 1.600 |
| $Cl_2$ after $SO_2$ | 100 | — | — | 1.03 | 15.7 | 0.524 |
| | 150 | — | — | 0.79 | 12.0 | 0.008 |
| | 200 | — | — | 0.71 | 10.7 | 0.511 |

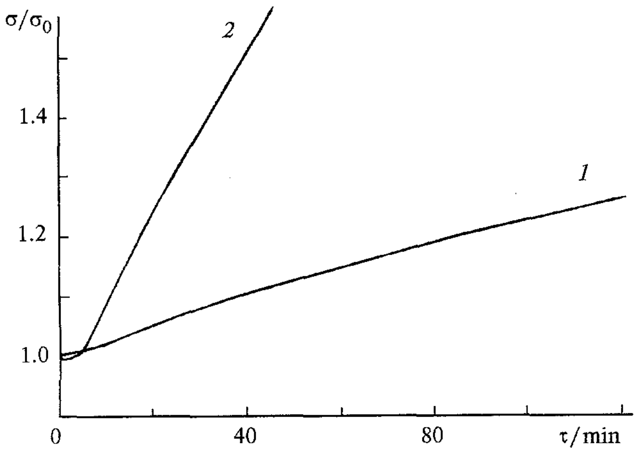

**Fig. 2.** The time variation of the relative electrical conductivity of $In_2O_3$ during chemisorption of $SO_2$ on a surface containing $Cl_2$: 100 °C (*1*), 150 °C (*2*).

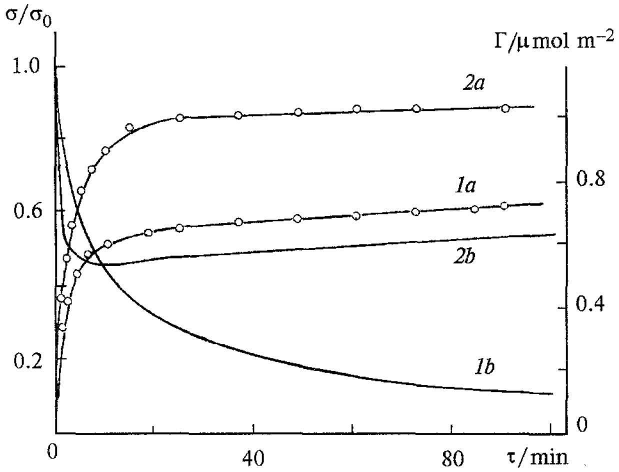

**Fig. 3.** The amount of gas sorbed (*a*) and the variation of the electrical conductivity (*b*) during chemisorption of $Cl_2$ on $In_2O_3$ at 100 °C: pure surface (*1*); surface containing $SO_2$ (*2*).

Although $Cl_2$ is sorbed in the dissociative form and each molecule occupies two adsorption sites, a molecule of $SO_2$ occupies only one active site.

At the same time, in contrast to sorption on the $Cl_2$-free surface, in the case of consecutive sorption, the amount of $SO_2$ chemisorbed increases with an increase in the temperature, which is typical of activated chemisorption. The character of the charge of the $In_2O_3$ surface also changes. In the presence of $Cl_2$, sorption of $SO_2$ is accompanied by a substantial increase in the conduction of $In_2O_3$ (Fig. 2); at 100 °C, 130 min after the beginning of the sorption, this increase is as high as 30 %. At higher temperatures, the increase in the conductance occurs more quickly.

It is known that $SO_2$ may be chemisorbed both in the donor and in acceptor forms, depending on the state of the oxide surface.[6,7] In the presence of $Cl_2$, $SO_2$ is sorbed in the donor form, which may be due to variation in the coordination of the $SO_2$ molecules on the surface. In the presence of chlorine, $SO_2$ is probably sorbed on the acidic sites of the surface to give $SO_3$ complexes, which is supported by the data of mass spectral analysis of the desorption products.

The chemisorption of $Cl_2$ at 100 °C on a $In_2O_3$ surface containing sorbed $SO_2$ occurs at a higher rate than that without $SO_2$, and the quantity of the $Cl_2$ sorbed is 40 % higher (see Table 1). No displacement of $SO_2$ from the surface to the gas phase is observed. When the temperature of sorption is increased to 150 and 200 °C, the amount of the consecutively sorbed $Cl_2$ decreases and becomes lower than that sorbed on a surface containing no $SO_2$.

The preliminary sorption of $SO_2$ exerts an effect on the character of the variation of the conductance. The chemisorption of $Cl_2$ on $In_2O_3$ at 100 °C was accompanied by a monotonic decrease in the conductance, which was the most pronounced in the initial period of sorption (up to three minutes), and the chlorine was desorbed unchanged.[3] In the case when the oxide surface contained $SO_2$, the initial decrease in the conductance was considerably smaller than that without $SO_2$. At 100 °C, the rapid decrease in the conductance was followed by its slow growth (Fig. 3), which continued after the sorption of chlorine was completed.

In the chemisorption of $Cl_2$ at 150 and 200 °C, an increase in the conductance was also observed without the preliminary sorption of $SO_2$. It has been found previously[3] that the increase in the conductance is caused by the formation of indium trichloride on the surface. In the case of the consecutive chemisorption of $SO_2$ and $Cl_2$ (100 °C), in addition to $InCl_3$, $SO_3$ and $SO_2Cl_2$ were also detected among the products of desorption.

An analysis of the results obtained showed that the regularities of the chemisorption of $SO_2$ on $In_2O_3$ are determined by the state of the surface layer of the oxide. In the absence of $Cl_2$, the chemisorption of $SO_2$ on $In_2O_3$ is nonactivated and the surface does not become charged. Preliminary chemisorption of $Cl_2$, which causes a decrease in the concentration of free electrons in the surface layer of the oxide, results in a change in the form of the $SO_2$ sorbed, as indicated by the increase in the conductance of the oxide.

When the order of the sorption is changed ($Cl_2$ after $SO_2$), chemisorption is complicated by the formation of the products of chlorination, which are formed at lower temperatures in the presence of $SO_2$ than in the absence of $SO_2$. One may suggest that redistribution of the electron density in the surface layer of the oxide, which accompanies binding of the surface oxygen to $SO_3$ groups, facilitates the chemisorption of chlorine, cleavage of the indium—oxygen bond, and the formation of the chloride. However, the possibility of chlorination of the surface by $SO_2Cl_2$, which was observed by mass spectrometry, cannot be ruled out.

In the absence of $SO_2$, the formation of chlorination products was noted only above 150 °C. With the preliminary sorption of $SO_2$, the concentration of these products on the surface increases. The fact that the oxide surface is occupied by the reaction products probably leads to a decrease in the amount of chlorine sorbed at 150—200 °C.

Thus, the studies of the chemisorption of $Cl_2$ and $SO_2$ on $In_2O_3$ and of the change in the electrical conductivity of the oxide have shown that the character of the interference of these gases depends on the order in which they are sorbed. Modification of the oxide surface prior to the chemisorption of a gas results in a change in the reactivity of the solid. Chlorides formed at lower temperatures during the chemisorption of $Cl_2$ on a surface with $SO_2$ than on $SO_2$-free surface. The preliminary chemisorption of $Cl_2$, in turn, caused changes in the charge of the surface during the subsequent adsorption of $SO_2$.

## References

1. A. A. Vinokurov, L. E. Derlyukova, and V. I. Evdokimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1927 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1751 (Engl. Transl.)].
2. A. A. Vinokurov, V. V. Ganin, L. E. Derlyukova, and A. V. Baluev, *Zh. Neorgan. Khim.*, 1990, **35**, 2302 [*Russ. J. Inorg. Chem.*, 1990, **35** (Engl. Transl.)].
3. M. V. Vinokurova, L. E. Derlyukova, A. A. Vinokurov, V. V. Ganin, and V. I. Evdokimov, *Zh. Neorgan. Khim.*, 1991, **36**, 2480 [*Russ. J. Inorg. Chem.*, 1991, **36** (Engl. Transl.)].
4. S. Z. Roginskii, *Geterogennyi kataliz* [*Heterogeneous Catalysis*], Nauka, Moscow, 1979 (in Russian).
5. N. I. Puzynina, Yu. P. Kuznetsov, and E. S. Petrov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 47 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, No. 1 (Engl. Transl.)].
6. S. A. Kent, J. P. Katzer, and W. H. Manoque, *Ind. Eng. Chem. Fund.*, 1977, **16**, 443.
7. V. I. Lygin, R. E. Tugushev, and I. K. Kuchkaeva, *Zh. Fiz. Khim.*, 1979, **53**, 2923 [*Russ. J. Phys. Chem.*, 1979, **53** (Engl. Transl.)].
8. A. A. Vinokurov, L. E. Derlyukova, and V. I. Evdokimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1449 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1337 (Engl. Transl.)].

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