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# The Claus Reaction:
# VI. The Reaction Mechanism over a Sn–Mo Oxide Catalyst

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**Abstract**—Based on the comparison of reactant conversions in pulses on the stationary surface of the catalyst, the Claus reaction is found to occur via a stepwise mechanism. The nature of interaction of the $SO_2$ and $H_2S$ molecules with the catalyst surface was studied by FTIR and UV–VIS spectroscopy and the reactivity of the adsorbed species was studied *in situ*. The intermediate adsorbed reactant species are determined. A scheme of the reaction mechanism over the Sn–Mo oxide catalyst is discussed.

## INTRODUCTION

Earlier [1–5] one of us showed that the Sn–Mo oxide catalyst (Sn : Mo = 9 : 1), which is a solid solution of molybdenum ions in $SnO_2$, is highly efficient and promising for the Claus reaction:

$$SO_2 + H_2S \longrightarrow S_x + H_2O.$$

It is important that the catalyst was stable even in the presence of oxygen in the reaction mixture, whereas well-known catalysts for this reaction, for example, $Al_2O_3$, are deactivated in the oxygen medium or in the presence of oxygen admixtures.

In this work, we attempted to elucidate the mechanism of this commercially important reaction using catalytic tests, UV–VIS and precision FTIR spectroscopy, including dynamic *in situ* measurements.

## EXPERIMENTAL

*Catalyst.* The Sn–Mo oxide catalyst (9 : 1) prepared by coprecipitation had a specific surface area of ~120 $m^2/g$ after drying for 10 h at 373 K followed by calcination in air for 4 h at 723 K and represented a solid solution of molybdenum ions in the $SnO_2$ lattice (according to XRD). The surface of this solid solution, according to the data of X-ray electron spectroscopy, is enriched in molybdenum ions (Sn : Mo = 4 : 1) [6, 7]. As IR-spectroscopic studies showed, a compound formed on the surface of the solid solution, as is a polymolybdenum (possibly heteropolymolybdenum) system with a typical spectrum (Fig. 1) [8]. As follows from further consideration below and findings reported in [7, 9], this system mostly contains two-dimensional compounds of six-coordinated molybdenum ions bound to the support surface. Nearly all Mo=O bonds are accessible to the adsorption of at least water and $NH_3$. The absorption band with a maximum at ~1010 $cm^{-1}$ shifts to 950 $cm^{-1}$ upon such interactions, and this indicates that the polymolybdenum compounds are not bulk. When this polymolybdenum compound is reduced, the support becomes "open" and accessible to adsorption.

*Catalytic tests*. The catalytic activity of samples in the Claus reaction was tested in a steel–glass flow-circulation setup held under a constant temperature of 403 K. Experiments were performed at 523 K and $H_2S$ and $SO_2$ concentrations of 0.5 and 0.25 vol %, respectively. The partial pressure of sulfur was 6.7 Pa. The circulation factor was 130 at a linear flow velocity of 8 m/s. Variation of the circulation factor showed that the effect of external diffusion on the rate was negligible. Samples with particle sizes of 0.25–0.5 mm were studied. Variation of the particle size from 0.25 to 3.0 mm showed that, for the particles with the size 0.25–0.5 mm, the reaction occurred in the kinetic region. The specific reaction rate was expressed as the number of the $H_2S$ molecules based on the unit of the catalyst surface area ($cm^2$). Before each run, the samples were activated by heating at 673 K in a helium flow for 2 h. The catalytic activities in the Claus reaction were compared at the following concentrations of reac-

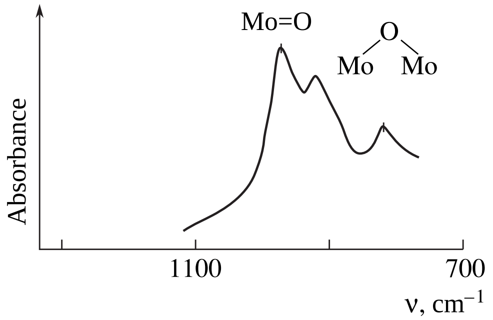

**Fig. 1.** IR spectrum of the Sn–Mo oxide catalyst in the region of inherent vibrations recorded in KBr pellets with compensation by the $SnO_2$ sample.

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tants in the cycle (vol %): $H_2S$, 0.5 and $SO_2$, 0.2. To compare the reaction rates over various oxide systems, the testing conditions were chosen to be similar to those described in [10] and used in the study of the catalytic activity of simple metal oxides in $H_2S$ oxidation with oxygen and sulfur dioxide.

Chromatographic analyses of $H_2S$, $O_2$, $SO_2$, and $H_2O$ in both initial and final mixtures were carried out using Porapak Q with helium as a carrier gas.

The conversions of sulfur compounds to elemental sulfur were calculated according to the equation

$$X_S = ([H_2S]_0 - [H_2S]_c) + ([SO_2]_0 - [SO_2]_c)/[H_2S]_0 + [SO_2]_c, \quad (1)$$

where $[H_2S]_0$ and $[SO_2]_0$ are the initial concentrations of the gases and $[H_2S]_c$ and $[SO_2]_c$ are their concentrations in the reaction cycle (mol/l). The conversions of $SO_2$ and $H_2S$ were determined similarly.

The pulse technique in a flow system was used to study *the reaction mechanism*. The conversions of both reactants ($SO_2$ and $H_2S$) on a stationary catalyst surface were estimated by the pulses of mixtures with the following compositions: (*1*) $H_2S + SO_2 + He$; (*2*) $H_2S + He$; and (*3*) $SO_2 + He$. The steady state of the catalyst was reached by the treatment of the catalyst with the reaction mixture in a flow system for 10 h. The small $H_2S$ and $SO_2$ concentrations in the $H_2S + He$ and $SO_2 + He$ pulses were chosen to minimize changes to the steady state. The portions of $H_2S$ converted in the pulse were, as a rule, less than 1% of the monolayer even at the maximum possible conversion. The number of molecules in each pulse was chosen to be much less than that of the surface atoms. Hence, the $H_2S$ and $SO_2$ concentrations in the $H_2S + He$ and $SO_2 + He$ pulses were low. They were preliminarily calculated taking into account the weight of the catalyst in the reactor. Therefore, the amount of surface atoms (in percent of a monolayer) interacted with $H_2S$ ($SO_2$) (Fig. 2) was calculated as the difference between the amounts of the reaction product in the adsorption layer and in the reactant pulse.

To study *the IR spectra of adsorbed molecules*, catalyst samples were pressed into pellets with a density of 60–100 mg/cm$^2$ and then placed in a special cell that allowed sample treatment at high temperatures (up to 773 K), as well as adsorption and desorption of gases at different temperatures. The cell was connected to a vacuum setup enabling a vacuum of up to $10^{-5}$ Torr. The IR spectra were recorded on a FTS Nicolet instrument. The concentration of the adsorption sites was estimated from the IR spectral absorbance of the adsorbed probe molecules such as CO, $NH_3$, and $CO_2$. Extinctions for these molecules were taken from the literature [11–13].

*The UV–VIS spectra* were measured on Shimadzu UV-300 and UV-160 spectrometers in the transmission and reflection modes with compensation of the spectrum of a support and with the use of an attachment for diffuse reflectance measurements. Measurements were carried out in a special sealed quartz cell that allowed sample training at temperatures up to 1273 K in an atmosphere of various gases and in a vacuum, as well as adsorption and desorption of gases and vapors under various conditions. Spectra were recorded at 293 K.

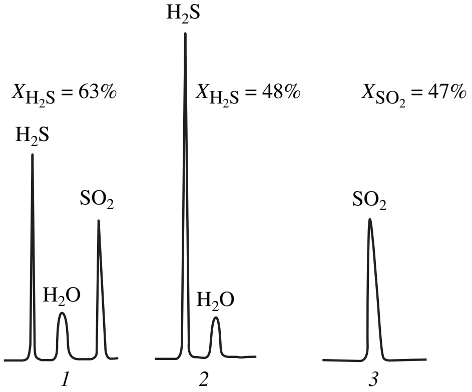


**Fig. 2.** Chromatograms and calculated conversions of $SO_2$ and $H_2S$ on the stationary surface of the Sn–Mo oxide catalyst at combined (*1*) and separate (*2*, $H_2S$; *3*, $SO_2$) pulse feed of reactants. $[H_2S] = 0.175$ vol %, $[SO_2] = 0.09$ vol %; $T = 523$ K. The portion of $H_2S$ converted in the pulse is 14% of the monolayer.

## RESULTS AND DISCUSSION

### *1. Determination of Reaction Stages*

It is known [14] that a pulse technique with a chromatographic analysis of the reactants provides information on whether the process occurs via a concerted mechanism or through the separate interaction of reactants with the catalyst. The mechanism with separate interaction takes place when the interaction rates (conversions) of reactants with a stationary catalyst surface are the same and equal to the reaction rate and the conversions of all reactants are close to those under separate interaction. The concerted mechanism takes place when the interaction rates (conversions) of reactants and their mixtures are different, that is, the presence of both reactants is necessary for the reaction to occur efficiently.

Comparison of the $H_2S$ and $SO_2$ conversions over a steady Sn–Mo oxide catalyst under both a combined and separate feed of $H_2S$ and $SO_2$ is illustrated by Fig. 2. As can be seen, the conversions of the reactants in the combined and separate pulses are close (for example, for $H_2S$ they are 63 and 48%, respectively) despite the high portion of the $H_2S$ monolayer converted in the pulse. Over catalysts on which the concerted mechanism is effective ($Al_2O_3$ and $TiO_2$), the conversions of the reactant (for example, $H_2S$) in the combined and separated pulses differs substantially

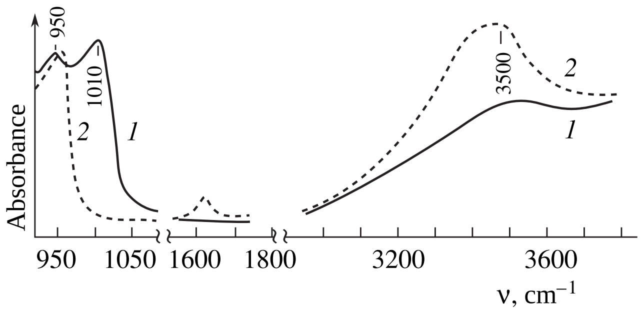


**Fig. 3.** IR spectra of the Sn–Mo oxide catalyst (*1*) oxidized at 723 K and (*2*) after interaction with water at 293 K.

(for example, over $TiO_2$ they are 95 and 23%, respectively). This is evidence that the process over an Sn–Mo oxide catalyst occurs via the mechanism of the separated interaction of the reactants with the catalyst. Note that the reaction product, $H_2O$, is completely evolved at the stage of the interaction with $H_2S$. Hence, we can suggest that over an Sn–Mo oxide catalyst, the Claus process occurs via the stepwise mechanism.

To elucidate the stages of this mechanism in detail and the nature of activation of the reacting molecules at a molecular level and to determine the nature and properties of the adsorption sites on the catalyst surface, spectroscopic experiments were performed.

### *2. IR-Spectroscopic Study of the Interaction of $H_2S$ with $SO_2$*

*Nature of adsorption sites.* Because the surface sites determine the adsorbed species of reactants and the routes of their transformations, let us first consider the nature of these sites. The nature of the surface sites on initial oxidized Sn–Mo oxide catalysts is determined by a polymolybdenum compound formed on the surface of the solid solution of molybdenum oxide in tin dioxide. In the IR spectrum of the sample preliminarily dehydrated at 723 K and oxidized in oxygen at 723 K, the absorption band at ~1010 cm$^{-1}$ is seen at frequencies higher than those of the proper absorption of the sample (Fig. 3, spectrum *1*). This absorption band is undoubtedly due to the vibration of the $Mo^{6+}$=O bond in the light of data analyzed in [9] and was not found in the spectrum of the initial sample in air. Only its shift to a low-frequently region (960–970 cm$^{-1}$) is seen, where the vibration of the Mo=O bond in the hydrated polymolybdenum compound is observed (Fig. 1). The variations in the spectrum of the sample are due to the interaction of the $Mo^{6+}$=O groups with water molecules, as can be seen from changes in spectrum *1* (Fig. 3) after water adsorption (Fig. 3, spectrum *2*). The absorption bands in the region of lower frequencies, 800–1000 cm$^{-1}$, characterize the vibrations of the Sn–O–Mo, Mo–O–Mo, and probably $Mo^{5+}$=O bonds. The presence of the $Mo^{5+}$ ions in the oxidized sample of the Sn–Mo oxide catalyst has been found by ESR and X-ray electron spectroscopies [6].

IR spectroscopic data for adsorbed probe molecules such as CO, $CO_2$, and $NH_3$ indicate that the polymolybdenum compound formed upon oxidation on the surface of the solid solution of molybdenum oxide in tin dioxide is characterized by the presence of Brønsted ($\delta_s(NH_4^+)$ = 1445 cm$^{-1}$) [15] and strong Lewis ($\delta_s(NH_3)$ = 1260 cm$^{-1}$, $\delta_{as}(NH_3)$ = 1610 cm$^{-1}$) acid sites, which are most likely $Mo^{6+}$ ions, because $Mo^{5+}$ ions are located predominantly in the bulk of the solid solution [7]. This compound covers the whole $SnO_2$ surface ($Mo/SnO_2$). The surface OH groups of $SnO_2$, the $Sn^{4+}$ cations detectable by adsorption of $NH_3$ ($NH_3$ ($\delta_s(NH_3)$ = 1240 cm$^{-1}$) and CO, and basic $O^{2-}$ ions detectable by $CO_2$ adsorption were not found in the IR spectra. The polymolybdenum compound in the oxidized state has only weak basic sites, which cannot stabilize $CO_2$ as carbonates. The molybdenum cations in the highest ($Mo^{6+}$) oxidation degree (hard acid) do not coordinate molecules of soft bases, such as CO (the ionization potential (IP) is 14.1 eV), NO (9.25 eV), and $C_3H_6$ (9.73 eV), but coordinate a hard base–$NH_3$. We assume that the $Mo^{6+}$ ions are probably "immersed" in the oxygen environment, that is, are not accessible to weak electron-donor molecules (CO, $C_3H_6$, and NO), whereas the molecules of the strong electron-donor $NH_3$ capable of forming a strong bond can "extract" Mo cations from the oxygen environment to the surface to form complexes. Hence, this phenomenon is the so-called structural nonrigidity of the surface [16].

After reduction in hydrogen at 573–673 K, a portion of the surface of $SnO_2$ (solid solution of Mo ions in $SnO_2$) becomes open. As a result, the absorption bands in the 1200–1700 cm$^{-1}$ region characterizing carbonates appear in the IR spectrum of adsorbed $CO_2$, and the absorption band at 1240 cm$^{-1}$ is observed in the spectrum of adsorbed ammonia and is due to ammonia coordinated to the $Sn^{4+}$ ions. Reduced molybdenum ions on the $SnO_2$ surface are characterized by $\delta_s(NH_3)$ = 1190 cm$^{-1}$ (most likely $Mo^{4+}$) and 1210 cm$^{-1}$ ($Mo^{5+}$). It is typical of the reduced polymolybdenum compound that molybdenum ions in the $Mo^{4+}$ state appear, which coordinate CO to form the $Mo^{4+}(CO)$ complex (absorption bands at 2180 cm$^{-1}$) and NO (four absorption bands are found, which, according to [17], indicate the formation of $Mo^{4+}(NO)$ and $Mo^{5+}(NO)_2$ dinitrosyl complexes). The Brønsted acid sites are not typical of this catalyst.

*Interaction with $H_2S$.* The intense interaction of the oxidized surface of the Sn–Mo oxide catalyst with $H_2S$ occurs at room temperature and is accompanied by a substantial decrease in the intensity of the absorption band at ~1010 cm$^{-1}$ up to the complete disappearance of this band and other absorption bands in the 800–1000 cm$^{-1}$ region, which characterize the Mo–O bonds. Simultaneously, the absorption band at ~950 cm$^{-1}$ and

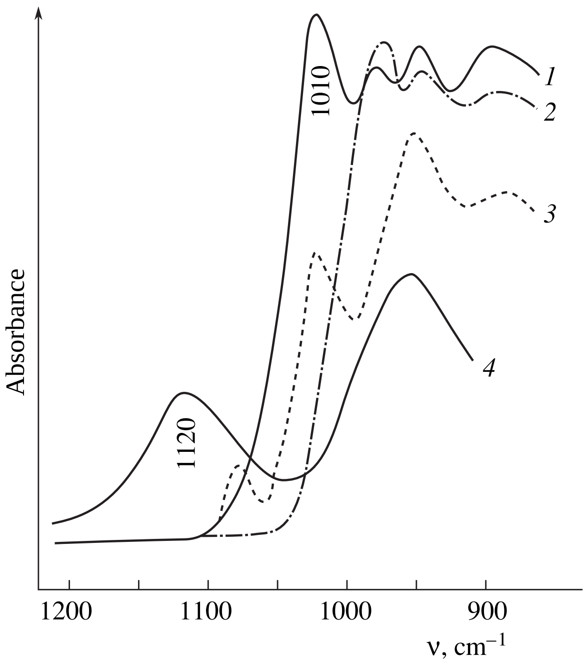


**Fig. 4.** IR spectra of (*1*) initial Sn–Mo oxide catalyst oxidized at 723 K; (*2*) after treatment with water at 293 K; (*3*) after reduction with $H_2$ at 523 K followed by evacuation at 673 K; and (*4*) after treatment with $H_2S$ (10 Torr) at 298 K for 30 min.

the new absorption bands at 1120 and 1620 cm$^{-1}$ appear (Fig. 4, spectrum *3*). Taking into account a marked increase in the absorption in the region of ν(OH) = 3200–3800 cm$^{-1}$ upon the $H_2S$ admission onto the sample of the Sn–Mo oxide catalyst, the band at 1620 cm$^{-1}$ most likely belongs to the bending vibrations (δ) of the water molecules formed upon the interaction of hydrogen sulfide with the oxidized catalyst surface. Special experiments on water adsorption on both oxidized and reduced Sn–Mo oxide catalyst confirmed this assignment.

Note that the removal of water molecules from the catalyst surface by deep evacuation at room temperature (the adsorption band at 1620 cm$^{-1}$ disappears from the spectrum, indicating the desorption of all water molecules within the accuracy limit of the method) does not restore the absorption band at ~1010 cm$^{-1}$ in the spectrum (this region of the spectrum practically does not change upon evacuation). In our opinion, this indicates that Mo=O groups participate in the reaction with hydrogen sulfide. It is obvious that a shift of the Mo=O absorption band is not due to the ligand effect of the water molecules formed during the reaction. It is most likely that, during the interaction of $H_2S$ with the Sn–Mo oxide catalyst, direct exchange of the sulfur atom of the hydrogen sulfide molecule with the oxygen atom on the surface of the oxide occurs to form water and a sulfide ion:

$$H_2S + (O^{2-}) \longrightarrow H_2O + (S^{2-}).$$

Such a reaction, first of all, occurs with the participation of the Mo=O and possibly Mo–O–Mo groups. This reaction causes the disappearance of the absorption band at 1010 cm$^{-1}$ from the spectrum upon the hydrogen sulfide adsorption. (It is difficult to follow the other absorption bands belonging to the polymolybdenum compound, although the intensities of all the bands characterizing the Mo–O bonds decrease.) The formation of molybdenum sulfide in this two-dimensional phase of the polymolybdenum compound is hardly probable since, according to the quantitative data obtained, not even all the oxygen atoms of the polymolybdenum compound are replaced by sulfur. The formation of the $MoS_2$ phase found in [15] may be due to the destruction of the solid solution because of severe conditions of the catalyst treatment with hydrogen sulfide employed in that work, as well as to the formation of $MoS_2$ and the involvement of all molybdenum ions. Note that the interaction of hydrogen sulfide with the surface of the Sn–Mo oxide catalyst at moderate temperatures does not lead to spectral evidence for $H_2S$ adsorption. When $H_2S$ is adsorbed on oxides (e.g., $Al_2O_3$ [18, 19]) the absorption bands usually appear in the region of stretching vibrations (νSH) ~ 2500–2600 cm$^{-1}$. In contrast to $Al_2O_3$, these bands were not found in the case of the Sn–Mo oxide catalyst apparently because of complete $H_2S$ dissociation on the surface of this catalyst.

In our opinion, the appearance of the absorption band at ~1120 cm$^{-1}$ in the spectrum of the Sn–Mo oxide catalyst after the interaction with $H_2S$ (Fig. 4, spectrum *4*) is due to the vibrations of ν(S=O) bonds formed by the oxidation of a small portion of the hydrogen sulfide molecules on the surface of the catalyst under study. The structure corresponding to this absorption band does not decompose upon evacuation; therefore, irreversible adsorption takes place, which is typical of the S=O bonds [20]. It is difficult to describe this adsorbed species in more detail. Hence, the findings of the studies show that, in contrast to the acid–base catalysts ($Al_2O_3$ or $TiO_2$) on which dissociation mostly occurs via only one S–H bond of hydrogen sulfide, on a redox Sn–Mo oxide catalyst both S–H bonds dissociate with the incorporation (substitution) of $S^{2-}$ ions into the catalyst and the evolution of water.

*The participation of surface sites in the $H_2S$ adsorption.* The treatment of the oxidized catalyst with hydrogen sulfide at 293 K causes a significant decrease in the concentrations of both Lewis and Brønsted acid sites, as follows from the corresponding changes in the spectrum of adsorbed ammonia. After the interaction at 573 K, the concentrations of acid sites decrease 10 times. Such changes in the site distribution confirm the above scheme for the $H_2S$ interaction with the catalyst surface. These changes may be due to the reduction of the polymolybdenum compound upon interaction with hydrogen sulfide, when the compound loses the Brønsted sites, as mentioned above (a phenomenon usually observed during the reduction of the surface

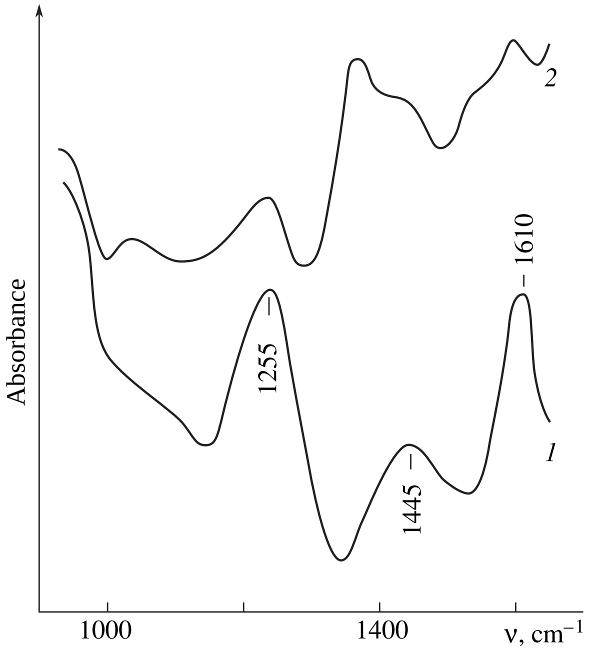


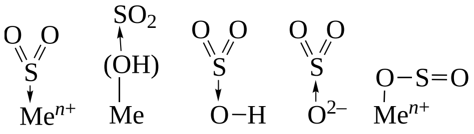
**Fig. 5.** IR spectra of ammonia adsorbed on the oxidized surface of the Sn–Mo oxide catalyst (*1*) before and (*2*) after interaction with $H_2S$.

Mo species [11]). Another reason is that the formation of new “rigid” Mo–S bonds in the structures similar to $MoS_2$ (more “rigid” than the Mo–O bonds in $MoO_3$) makes the incorporation of ammonia into the coordination sphere of the molybdenum ions impossible. In the spectra of $NH_3$ adsorbed on this catalyst, the absorption bands of ammonia coordinated by both reduced molybdenum ions ($\delta_s(NH_3)$ = 1190, 1210 $cm^{-1}$) and $Mo^{6+}$ ions ($\delta(NH_3)$ = 1260 $cm^{-1}$) were not found. At the same time, the $Sn^{4+}$ ions coordinate ammonia molecules (the absorption band $\delta_s \sim 1240$ $cm^{-1}$) (Fig. 5).

Note that few Brønsted sites remain on the surface of this catalyst even upon high-temperature and repeated treatment with $H_2S$ (Fig. 5, spectrum *2*). However, the presence of the Brønsted sites in the samples can be due to both the molybdenum ions in the highest oxidation states, as in the case of the oxidized sample, and to the appearance of the Brønsted sites on the $SnO_2$ surface due to its modification with ions $SO_4^{2-}$. The ions are probably formed in a small amount on the surface of the polymolybdenum compound and migrate to the support upon reduction, thus modifying the support and giving rise to the formation of proton centers, which were found, for example, in $TiO_2$ doped by $SO_4^{2-}$ ions [21].

*Interaction with $SO_2$.* After $SO_2$ adsorption at room temperature on the oxidized surface of the Sn–Mo oxide catalyst, the absorption bands at 1140 and 1340 $cm^{-1}$ appear in the spectrum, which characterize reversible adsorption, since the structure corresponding to these absorption bands decomposes due to desorption at room temperature. Irreversible adsorption, which is characterized by the absorption bands at ~1080 and 1100–1140 $cm^{-1}$ (Fig. 6, spectrum *2*), is observed simultaneously. This adsorbed species does not decompose upon desorption up to high temperatures, and the absorption bands at ~1080 and 1100–1140 $cm^{-1}$, according to the earlier reported data on the $SO_2$ adsorption over oxides [22–26], most probably characterize ν(S=O) in both the sulfite and sulfate structures. Note that the concentrations of these compounds on the surface of the Sn–Mo oxide catalyst are not so high as that on MgO [25, 26] or $Al_2O_3$ [22–24], and this is undoubtedly due to the lower basicity of oxygen on the surface of the Sn–Mo oxide catalyst compared to MgO and $Al_2O_3$. The appearance of the $CO_2$ absorption bands in the IR spectrum of the oxidized Sn–Mo oxide catalyst also indicates the lower basicity of oxygen in the polymolybdenum compound. As mentioned above, $CO_2$ does not interact with the oxidized surface of this catalyst at 293 K, unlike $Al_2O_3$ and MgO, on which such interaction readily occurs under these conditions to form carbonates [13]. In the case of the Sn–Mo oxide catalyst, the interaction with the surface oxygen resulting in the formation of sulfite–sulfate structures is apparently due to the presence of the strong oxidation sites participating in the formation of the surface $SO_3^{2-}$ and $SO_4^{2-}$ groups. Certainly, it is necessary to take into account the stronger acidic properties of $SO_2$ compared to $CO_2$.

According to the reported UV–VIS and IR spectroscopic data [22–26] on the $SO_2$ adsorption on oxides, the following species can be formed upon the reversible $SO_2$ adsorption:



**I** **II** **III** **IV** **V**

Difficulties in the spectral identification of these compounds are due to their close thermal stability and symmetry, which determine the proximity of their spectral characteristics. Let us examine the possibility of the formation of each of these species, taking into account the nature and properties of the surface sites of this catalyst. The existence of basic hydroxyl groups on the catalyst surface is improbable. Clear absorption bands ν(OH) have not been found in the IR spectrum [7]. As a result, the formation of species **II** can be ruled out with a high probability. Compound **III** can be formed and contributes to the absorption bands, which characterize the reversible adsorption. However, this type of interaction cannot be preferred, because only the blocking of the surface basic sites by $CDCl_3$ substantially decreased the fraction of the reversible adsorption, whereas the treatment of the catalyst surface with NaOH resulting in the removal of the $H^+$ sites slightly affected the fraction of the reversible adsorbed species.

Note that the reversibly adsorbed species do not markedly affect the Mo=O bonds, since the absorption bands in the 900–1050 $cm^{-1}$ region and especially that at ~1010 $cm^{-1}$ characterizing $(Mo=O)^{3+}$ remain almost unchanged during the $SO_2$ adsorption–desorption cycles at room temperature. These data most probably indicate that $SO_2$ does not interact directly with either the oxygen or molybdenum ions forming these pairs. Taking into account the facts that CO, NO, and $C_3H_6$ do not interact with molybdenum cations in this oxidized catalyst ($Mo^{6+}$) and that the $C_3H_6$ (IP = 9.73 eV) and NO (IP = 10.2 eV) molecules are stronger donors than $SO_2$ (IP = 12.34 eV), it is unlikely that $SO_2$ interacts with the molybdenum ions. Meanwhile, reversible $SO_2$ adsorption is observed. Therefore, we can suggest that the most probable interaction in this case is $SO_2$ adsorption on the surface $O^{2-}$ basic sites in the Mo–O–Mo polymolybdenum compound and/or in the Mo–O–Sn fragments to form the donor–acceptor complex **IV**. As mentioned above, hydroxyl groups are absent from the surface of this catalyst, the molybdenum cations are inaccessible because of the low donor ability of $SO_2$, and the basicity of oxygen in the polymolybdenum compound is insufficient to form sulfites. In this case, it is clear that the interaction of the surface oxygen with $SO_2$ stops at the stage of complex **IV** formation. Taking into account the weak basicity of the polymolybdenum compound, one can assume that this adsorption is reversible and dominating. In our opinion, it is this species that is characterized by the absorption bands at ~1340 and 1140 $cm^{-1}$ ($\nu_3$ and $\nu_1$ are somewhat shifted relative to a free $SO_2$ molecule). The positions of these bands in the case of the Sn–Mo oxide catalyst are practically independent of the surface coverage with adsorbed $SO_2$. Taking into account the amphoteric properties of $SO_2$ (this molecule can act as both an electron-donor and electron-acceptor), the formation of stable $SO_2$ complexes with pyridine, trimethylamine, etc., and the IR spectroscopic characteristics of these complexes [27], the conclusion that complex **IV** is formed seems to be reasonable.

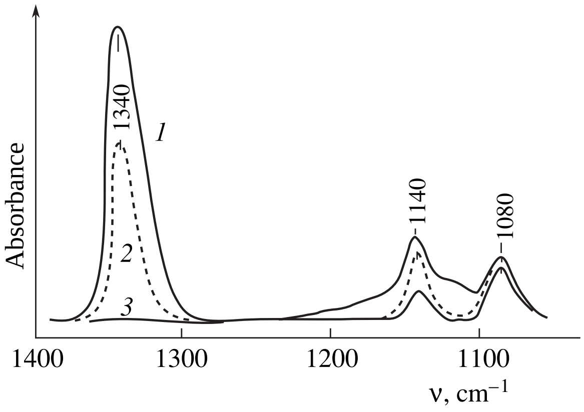
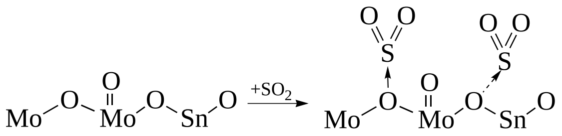


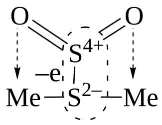
**Fig. 6.** IR spectra of $SO_2$ adsorbed on the oxidized surface of the Sn–Mo oxide catalyst after adsorption of $SO_2$ (*1*) 1 and (*2*) 10 Torr followed by desorption (*3*). $T$ = 298 K.

The data on $SO_2$ interaction with the sulfided surface of the Sn–Mo oxide catalyst are in good agreement with the above scheme for $SO_2$ interaction with the oxidized surface. As shown above, the interaction with $H_2S$ results in the reduction of the molybdenum ions and their complete blocking for adsorption of even such strong electron-donor ligands as ammonia, as well as in the appearance of $Sn^{4+}$ ions. The absorption band at ~1325 $cm^{-1}$ is probably due to the formation of the $Sn^{4+} \longleftarrow SO_2$ complexes at a small amount of $SO_2$ (1.8 μmol) adsorbed on this catalyst. Note that the position of this absorption band depends on the coverage. However, even with complete coverage (9 μmol), this absorption band is observed at 1330 $cm^{-1}$ rather than at 1340 $cm^{-1}$, as was found for the oxidized catalyst. This absorption band 1330 $cm^{-1}$ probably characterizes the complex of $SO_2$ with the surface $O^{2-}$ sites, which, as mentioned above, are more basic than the $O^{2-}$ ions of the polymolybdenum compound. It is obvious from the IR spectroscopic characteristics of $SO_2$ on MgO (in complex **I**, $\nu_3$ ~ 1320 $cm^{-1}$ [26]) that the $\nu_3$ value for this complex decreases with an increase in the basicity of the surface oxygen. The fact that $SO_2$ adsorption resulting in the $SO_3^{2-}$ and $SO_4^{2-}$ structures does not affect Mo=O groups can be explained by (i) the small concentration of strong oxidation sites in the catalyst under study, that is, low concentrations of $SO_3^{2-}$ and $SO_4^{2-}$ ions, and (ii) possible stabilization of such compounds by tin ions, that is, by the formation of such structures with the bridging oxygen atoms (in Mo–O–Sn or Sn–O–Sn fragments). These oxygen atoms are more basic than those in the Mo–O–Mo groups participating in the reversible adsorption, and this fact probably determines sulfite formation according to the scheme



It is obvious that a portion of molybdenum ions ($Mo^{6+}$, the absorption band of Mo=O at ~1010 $cm^{-1}$) should be reduced to at least $Mo^{5+}$ (the absorption band of $Mo^{5+}$=O at ~950 $cm^{-1}$). However, the concentration of the contact points for the polymolybdenum compound with the $SO_2$ surface, which are accessible to the interaction with $SnO_2$, is small. Moreover, the absorption bands of Mo=O bonds superimpose on the absorption bands of $SnO_2$ and the solid solution of $Mo^{5+}$ in $SnO_2$. As a result, all these facts may slightly affect the intensities of the corresponding absorption bands in the spectra.

*Interaction between $SO_2$ and adsorbed $H_2S$.* As mentioned above, the interaction of $H_2S$ with the surface of the Sn–Mo oxide catalyst results in the formation of the polymolybdenum hydroxysulfide compound in which the $O^{2-}$ ions are partially substituted for the $S^{2-}$ ions. A portion of the molybdenum ions is reduced to $Mo^{4+}$, and the adsorption on the support (solid solution of $Mo^{5+}$ in $SnO_2$), which is close to $SnO_2$ in adsorption properties, becomes possible. Sulfur dioxide reacts with the sulfided catalyst surface after evacuation at 373–473 K at rather low temperatures (293–372 K). It is obvious that water removal from the catalyst surface becomes possible at ~523 K and this surface becomes accessible to the interaction with $SO_2$. Correspondingly, the absorption bands at 1010 and 980–990 $cm^{-1}$ characterizing the $Mo^{6+}$=O and $Mo^{6+}$–O–$Mo^{6+}$ bonds appear in the IR spectra, and their intensities increase. Therefore, it is beyond question that this catalyst surface treated with $H_2S$ is oxidized by $SO_2$. Note that on both oxidized catalysts and those reduced with $H_2S$, adsorption was found in the IR spectrum after the consumption of 1.8 μmol $SO_2$, whereas on the sulfided catalyst, the absorption band at 1325 $cm^{-1}$ appeared only after the adsorption of 18 μmol. These findings, along with data on sulfur formation, undoubtedly indicate that $SO_2$ molecules are consumed for the surface oxidation and sulfur formation. This follows from an examination of the difference UV–VIS spectra of the sulfided Sn–Mo oxide catalyst before and after its interaction with $SO_2$. Absorption in the 300–400 nm region was found for these samples. According to the spectra of individual sulfur compounds [18], this absorption can only be due to the formation of sulfur compounds. Hence, these data give evidence that $S^-$ ions are the active sites for the interaction with the $SO_2$ molecules from the gas phase. As quantitative measurements show, interaction with $SO_2$ even at room temperature continues until the complete consumption of these sites. After this, the absorption band $\nu_3$ at ~1325 $cm^{-1}$ characterizing the vibrations of $SO_2$ molecules reversibly adsorbed on the support surface appears in the spectra and grows to a certain limit (clearly as a result of the small number of adsorption sites). The intensity of this absorption band does not change in time, indicating that this adsorbed species was not consumed. Special experiments on $SO_2$ adsorption on $SnO_2$ showed that this absorption band was also found when the $Sn^{4+} \longleftarrow SO_2$ and/or Sn–O $\longrightarrow SO_2$ complexes were formed. The formation of such complexes probably determines the appearance of this absorption band in the spectrum of the catalyst after interaction with $SO_2$. As mentioned above, the catalyst is reduced due to the interaction with $H_2S$, and the support surface becomes “open”, that is, accessible to interaction. The initial rate of the interaction with S evaluated by a decrease in the $SO_2$ concentration in time is ~$10^{13}$ mol $H_2S$ $cm^{-2}$ $s^{-1}$ at 523 K; that is, it exceeds the steady-state reaction rate on this catalyst. This indicates that the reaction can occur via this stage. The data obtained allow us to suggest that, in the precatalytic stage, the complex $S^{2-} \longrightarrow SO_2^*$ can exist (at least, such an interaction resulting in sulfur formation occurs), but it is impossible to observe it by IR spectroscopy at room temperature, probably because of the high rates of sulfur formation. This interaction of ($S^{2-}$) with $SO_2$, which is necessary for both surface oxidation and sulfur formation, becomes obvious in the experiments on the $SO_2$ interaction with the surface reduced with $H_2$. In this case, the reoxidation of the catalyst by $SO_2$ was not observed up to 573 K, whereas the catalyst treated with $H_2S$ reacts with $SO_2$ and its surface is reoxidized even at room temperature. In our opinion, the latter is due to the fact that the surface reoxidation is facilitated by the $SO_2$ interaction with sulfur:



**VI**

$SO_2$ adsorption at 298 K on the catalyst reduced with $H_2$ was observed in the IR spectra beginning from 2 μmol of adsorbed $SO_2$, since the $SO_2$ molecules did not react with $S^{2-}$.

*Interaction of adsorbed $SO_2$ with $H_2S$.* The dosed adsorption of hydrogen sulfide on the sample containing preliminarily adsorbed $SO_2$ allowed us to show that the intensities of the absorption bands at 1330 and 1140 $cm^{-1}$ corresponding to the reversible $SO_2$ adsorption rapidly decrease and completely disappear upon the adsorption of 3.3 μmol $H_2S$. Special experiments showed that the disappearance of these absorption bands is due to the interaction between $SO_2$ and $H_2S$ rather than the displacement of $SO_2$ from the surface. UV–VIS spectra of the catalyst after this interaction revealed the appearance of elemental sulfur on the surface. Absorption in the 300–400 nm region typical of the $S_2$–$S_8$ elemental sulfur and $S_{polymer}$ was found in these spectra [18], and this confirmed the explanation suggested above for the change in the absorption bands corresponding to the reversible $SO_2$ adsorption.

Figure 7 presents data on the reactivity of various species of adsorbed $SO_2$ toward $H_2S$. As can be seen, the reversibly adsorbed $SO_2$, which is characterized by the absorption band at 1330 $cm^{-1}$, is most reactive. The evaluation of the rate of the interaction of this adsorbed species with $H_2S$ showed that this species provides the occurrence of the Claus reaction at 523 K; that is, the initial interaction rate with $H_2S$ is even higher than the reaction rate.

*The Claus reaction mechanism.* As shown above, the reversibly adsorbed species, which is the donor-acceptor complex of $SO_2$ with the surface $O^{2-}$ ions, is

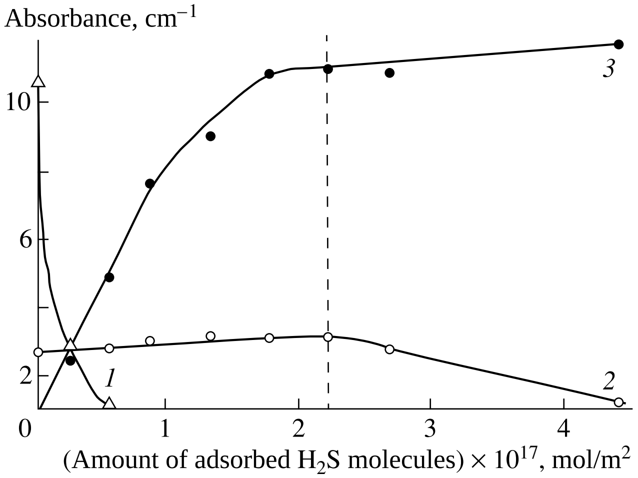


**Fig. 7.** Changes in the absorbance of the absorption bands of adsorbed $SO_2$ during interaction with $H_2S$ at 293 K: (*1*) 1330, (*2*) 1080, and (*3*) 1620 cm$^{-1}$.

the predominant adsorbed species on the oxidized surface of the Sn–Mo oxide catalyst. Hydrogen sulfide reacts with the surface of the Sn–Mo oxide catalyst to a greater extent to form new Mo–$S^{2-}$ bonds and water. The $S^{2-}$ groups that are stronger donors than the $O^{2-}$ ions readily react with the reversibly adsorbed $SO_2$ molecules and those from the gas phase to form elemental sulfur as a reaction product and to oxidize the surface. The reaction easily occurs when the water that is formed due to $H_2S$ adsorption and blocks the $S^{2-}$ sites is removed. Removing the water is not difficult and can be done by increasing the reaction temperature above 373 K, when the water begins to desorb. Hence, the redox electron transfer from $S^{2-}$ to $S^{4+}$ ions occurs during the interaction of $S^{2-}$ with $SO_2$. Simultaneously, the catalyst surface is reoxidized by the oxygen of $SO_2$ molecules. The energy released upon reoxidation can be utilized for the whole reaction; that is, the coupling of stages takes place. Thus, the interaction of $S^{2-}$ ions with the $SO_2$ molecules is obvious. The formation of elemental sulfur is accompanied by the reoxidation of the catalyst with the oxygen of sulfur dioxide. The data obtained indicate that over the Sn–Mo oxide catalyst, the Claus reaction occurs via the stepwise redox mechanism with coupled surface oxidation and sulfur reduction.

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