The Reaction between SO_2 and MnO_2 and the Role of the Sulfato Complex in the SO_2-induced Isomerization of *cis*-2-Butene

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The reaction between SO_2 and MnO_2 has been studied by measuring the consumption of SO_2-gas and the infrared spectra of the wafer of MnO_2. In the low-temperature range (<200 °C) the reaction is completed within one or two surface layers of MnO_2, and the reaction products are the bidentate sulfato complex (C_{2v}) and the sulfato complex in Td symmetry. In the high-temperature range, on the other hand, the reaction progresses deep into the bulk and can be described by this stoichiometric equation; $MnO_2+SO_2 \rightarrow MnSO_4$. The catalysis of MnO_2 for the SO_2-induced isomerization of *cis*-2-butene is closely related to the formation of the sulfate ion. The initiation step proposed for the isomerization is a polarization of the charge-transfer complex of SO_2 and butene under the influence of the strong electrostatic field caused by the generation of the surface sulfato complex.

The absorption of SO_2 from flue gas by an activated manganese oxide has become of interest in the field of SO_2-emission control.[1,2] In relation to this subject several kinetic studies of SO_2 absorption by manganese dioxide has been published.[3-5] However, no study of the chemistry of the reaction between SO_2 and manganese dioxide has been reported.

Otsuka *et al.* reported that, in the presence of SO_2, MnO_2 gains a very high catalytic activity in the cis-trans selective isomerization of various olefins, which is accompanied by copolymerization between SO_2 and olefins in the adsorption layer.[6] They hypothesized that the high catalytic activity of MnO_2 may be caused by a strong electrostatic field on the surface brought about by the formation of a sulfato complex.

The purpose of the present work is to investigate the reaction between SO_2 and MnO_2 by measuring the consumption of SO_2-gas and the infrared spectra of the wafer of MnO_2, and to verify the above hypothesis as to the high catalytic activity of MnO_2 in the copolymerization-accompanying isomerization of *cis*-2-butene.

Experiments

Materials. Commercial MnO_2 prepared by the reduction of $KMnO_4$ was used as the catalyst. The surface area, as determined by the BET method with nitrogen after degassing treatment at 100 °C, was 104 m^2/g. The $MnSO_4 \cdot 4$—$6H_2O$ was a product of Wako Pure Chemical Ind., Ltd. The reagent SO_2 gas, of an anhydrous grade and supplied by the Matheson Chemical Co., and the *cis*-2-butene gas, a high-purity product of the Phillips Petroleum Co., were purified by trap-to-trap distillation in a vacuum apparatus.

Procedure. The catalyst in the reactor was degassed in a vacuum for 2 h at 0 or 100 °C prior to each run. The amount of the consumption of SO_2-gas by MnO_2 was determined by measuring the pressure change by means of glass Boulden Gauge attached to a conventional glass apparatus with a volume of 320 ml. The polysulfone-accompanying isomerization of *cis*-2-butene was carried out in a conventional mercury-free gas-circulation system using a mixture of SO_2 and *cis*-2-butene (1:2.5) under a total initial pressure of 175 Torr. After the addition of SO_2 to 0.05 g of MnO_2 at a required temperature for 30 min under 50 Torr of SO_2, the temperature at the catalyst bed was decreased to 20 °C or to −10 °C; then, the two reactions (the copolymerization of SO_2 and *cis*-2-butene and the isomerization of the latter) were initiated by feeding in *cis*-2-butene and circulating the gas mixture through the catalyst bed. The rate of the cis-trans isomerization was determined from the concentration of the *trans*-2-butene formed in the initial 3 min, as analyzed by gas chromatography. The amount of the copolymer generated in the 30-min period after the initiation of the reaction was estimated by measuring the infrared-absorption spectra of the MnO_2 used for the reaction. Prior to the infrared-spectra measurement, the MnO_2 sample was ground to a fine powder, and then mixed with KBr. A KBr-supporting wafer was made by pressing the mixture in 2-cm-diameter stainless steel dies at 1.9 t/cm^2. The spectra were recorded at 25 °C using a Shimadzu IR-430 grating spectrometer.

Results and Discussion

SO_2-absorption Measurement by Volumetric Method. The changes in the amount of SO_2 absorbed by MnO_2 with the time have been shown in Fig. 1; the experiment was carried out by introducing 1.38×10^{-3} mol of SO_2-gas into the system. After the initial rapid absorption of SO_2 for 1 min, a small increase in the absorbed amount is observed at the temperatures lower than 200 °C, but significant amount of SO_2 are absorbed further at 250 and 350 °C in the range

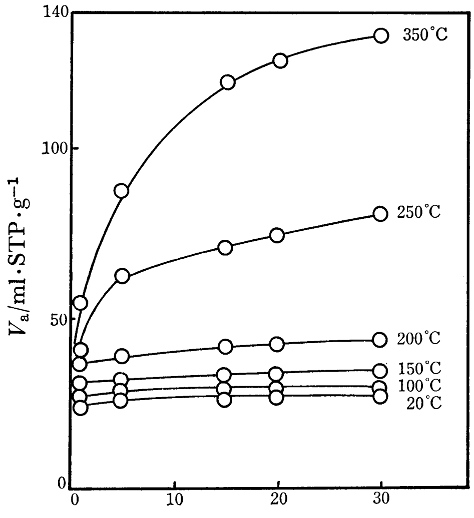


Fig. 1. Changes in the amount of SO_2 absorbed by MnO_2 with time at various experimental temperatures.

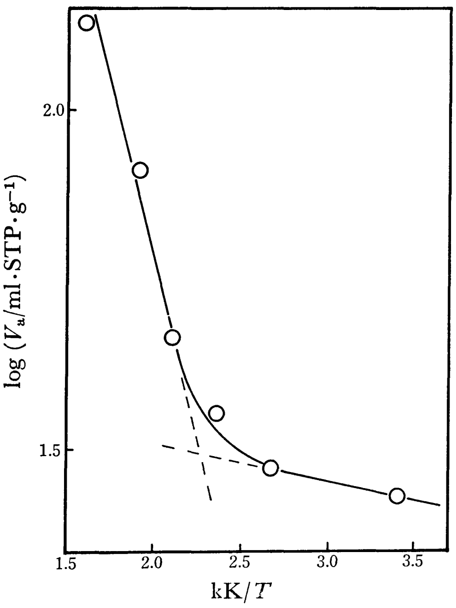


Fig. 2. log (V_a) against 1/T plot.

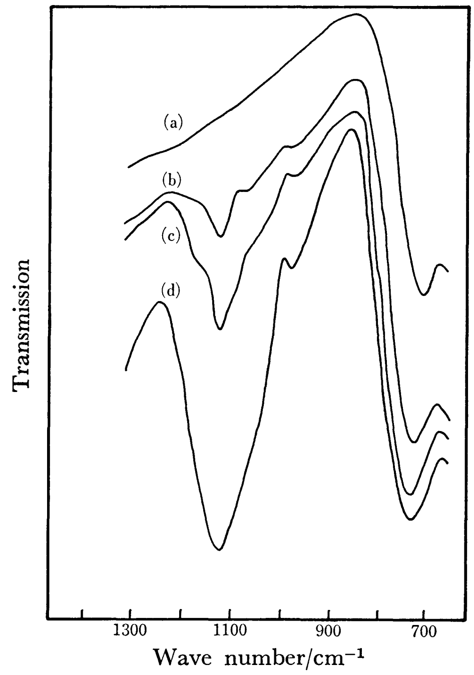


Fig. 3. Infrared spectra of the MnO_2 wafer with absorbed SO_2 at different θ_{SO_2}: (a); MnO_2 without SO_2, (b); MnO_2 with absorbed SO_2 (θ_{SO_2}=0.021), (c); θ_{SO_2}=0.21, (d); θ_{SO_2}=0.74. The SO_2 absorption was carried out at 20 °C with MnO_2 pretreated at 100 °C.

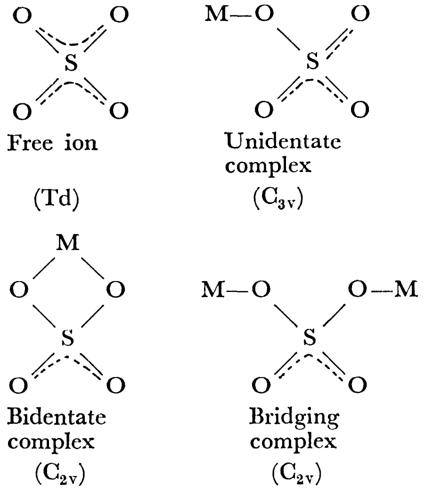
of the absorption time from 1 to 30 min. Figure 2 shows the log (V_a) against 1/T plot, where V_a is the amount of SO_2 absorbed in 30 min and where T is the absorption temperature in Kelvin. The quite different slopes of the curve in the low-temperature (<150 °C) and high-temperature ranges (>200 °C) in Fig. 2 suggest that the natures of the SO_2-absorption on MnO_2 are different between the two temperature ranges. The apparent surface coverage by SO_2, θ_{SO_2}, for various absorption temperatures was estimated from the amount of SO_2 absorbed in 30 min, and the BET surface area of the catalyst, from the nitrogen adsorption, where the molecular cross sections of N_2 and SO_2 were taken as 16.2 and 19.2 Å^2 respectively.[7] The results are summarized in Table 1. The large θ_{SO_2} values at the high temperatures listed in the table indicate that SO_2 penetrates into many layers of the surface.

Table 1. The apparent surface coverage by SO_2, θ_{SO_2}, for the MnO_2 used in the experiments of Fig. 1

Temperature (°C)	20	100	150	200	250	350
θ_{SO_2}	1.35	1.47	1.74	2.27	4.01	6.52

Infrared Spectroscopic Study of the Reaction of SO_2 with MnO_2. Figure 3 shows a series of changes in the spectra of the KBr-supporting wafer of the catalyst after the absorption of the required amount of SO_2 at 20 °C for 30 min. The preparation of the wafer and the recording of the spectra were carried out in air as has been described previously. To examine the effect of air on the spectra of the SO_2-absorbing catalyst, the spectra of the air-free sample deposited on the surface of the KBr-wafer, which has been placed in a vacuum cell, has been recorded. It has been confirmed that the introduction of air into the cell does not change the absorption bands caused by the addition of SO_2. The spectra of the catalysts with a low coverage ($\theta_{SO_2} < \approx 0.21$) show four absorption bands at around 980, ≈1070, 1115, and 1180 cm^{-1}. For the catalyst with θ_{SO_2} of 0.74, however, the absorption bands at ≈1070 and 1180 cm^{-1} are obscured by the selectively developed 1115 cm^{-1} band.

Nakamoto[8] indicated that the SO_4-complex in Td symmetry shows the ν_1(very weak), ν_3(very strong), and ν_4(strong) absorption bands at 973, 1130—1140, and 617 cm^{-1}. The lowering of symmetry for the SO_4-complex caused by coordination splits the ν_3 band into two or three bands, depending on whether the unidentate or bidentate and bridging complexes respectively are involved.



(1)

Many bidentate and bridging sulfato complexes, such as $[Cu(bpy)SO_4]\cdot 2H_2O$, $Pd(NH_3)_2SO_4$, and $[(NH_3)_4$-

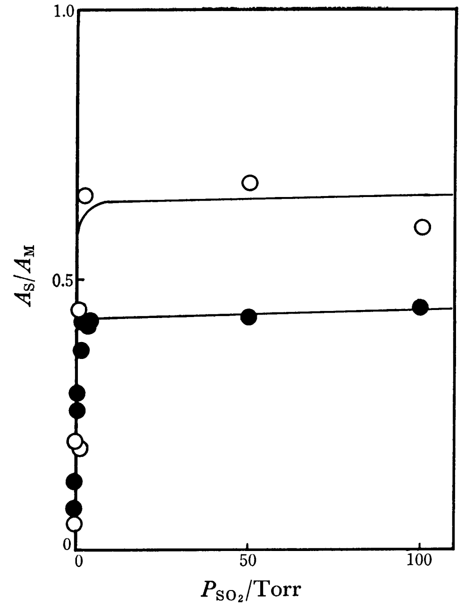


Fig. 4. Effect of SO_2-pressure on the relative amount of SO_4^{2-} complex formed at 20 °C: (○); MnO_2 degassed at 0 °C, (●); MnO_2 degassed at 100 °C.

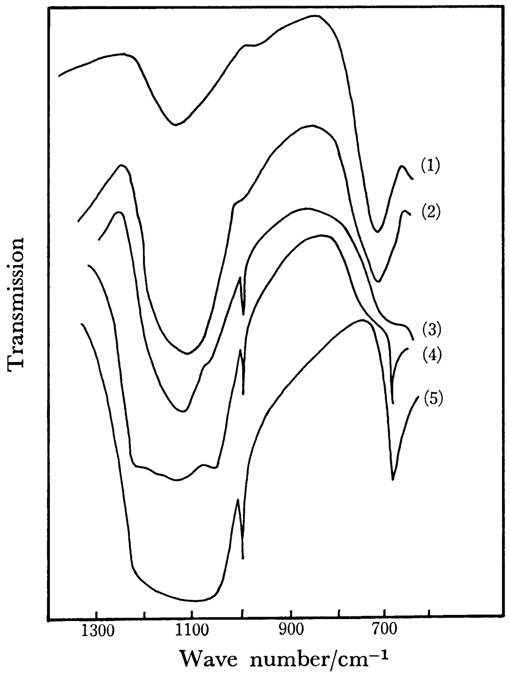


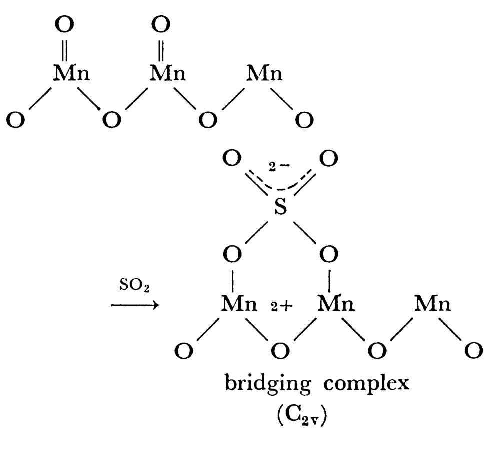
Fig. 5. Infrared spectra of SO_4-complex formed at different temperatures over MnO_2: (1); 20 °C, (2); 200 °C, (3); 300 °C, (4); 350 °C, (5); the spectra of $MnSO_4\cdot 4$—$6H_2O$.

$\mathrm{Co}\langle{}^{\mathrm{NH_2}}_{\mathrm{SO_4}}\rangle\mathrm{Co(NH_3)_4](NO_3)_3}$, show the three bands at 1030—1060, ≈1105, and ≈1180 cm^{-1}.[8] Hence, the spectra observed at a low θ_{SO_2} in Fig. 3 can be ascribed to the bidentate or bridging SO_4^{2-}-complex on MnO_2. On the other hand, the selective increase in the intensity of the band at 1115 cm^{-1} with an increase in θ_{SO_2} indicates that SO_4^{2-}-complex in Td symmetry is a main species formed at a high θ_{SO_2}. A_S/A_M, the optical density for the strongest absorption band at 1115 cm^{-1} divided by that for the 710 cm^{-1} band, caused by the Mn–O vibration in the MnO_2 lattice,[9] represents the relative amount of the SO_4^{2-}-complex on a unit weight of the catalyst. This value has been plotted in Fig. 4 as a function of the SO_2 pressure applied in the SO_2-absorption experiments at 20 °C for the catalysts degassed at 0 and 100 °C. The formation of the SO_4^{2-}-complex reaches a plateau at less than 1 Torr, and the amount of the SO_4^{2-}-complex formed is larger for the MnO_2 pretreated at a lower temperature.

Figure 5 shows the infrared spectra of the catalysts after SO_2 absorption under the same experimental conditions as those used to obtain the results in Fig.1. The relative amount of the SO_4^{2-}-complex increases as the absorption temperature is raised, accompanied by a decrease in the intensity of the 710 cm^{-1} band due to the Mn–O lattice vibration. The catalysts used for the experiment at the high temperatures (>300 °C) show spectra quite similar to that of $MnSO_4$. On the other hand, the spectra for the catalysts used for SO_2-absorption at low temperatures (<≈200 °C) do not show sharp bands at 1000 and 690 cm^{-1}, suggesting that the SO_4^{2-}-complex (Td symmetry) is different in its nature from the one observed on the catalyst used for the SO_2-absorption at high temperatures.

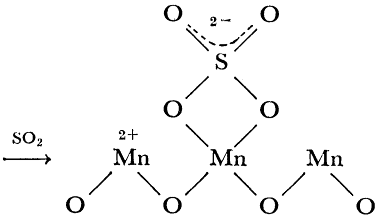
The results in Fig. 2 demonstrate that the reaction mechanism for the SO_2-absorption changes with the temperatures above ≈200 °C. At low temperatures, after a very rapid absorption of SO_2 within 1 min, only a small increment in the absorbed amount was observed (Fig. 1) and the amount of the SO_4^{2-}-complex formed did not change with the SO_2 pressure above 1 Torr (see Fig. 4). The apparent coverage of the surface by SO_2 remains less than 2.3 at low temperatures. These facts suggest that the progress of the reaction between SO_2 and MnO_2 at low temperatures (<≈200 °C) is restricted to only one or two surface layers of MnO_2. Accordingly, we consider that the initial stage of SO_2-absorption by MnO_2 may be demonstrated by the following schemes at low temperatures:

at a low θ_{SO_2},



(2)

or



(3)

bidentate complex
(C_{2v})

at a high θ_{SO_2},

$$MnO_2\ (\text{surface}) \xrightarrow{SO_2} \underset{(Td)}{SO_4^{2-}\text{-complex}}\ (\text{surface}) \qquad (4)$$

At high temperatures, the fact that the spectra observed are quite close to that of pure $MnSO_4$ (Fig. 5) indicates that SO_2 penetrates into the bulk of MnO_2 and forms $MnSO_4$ as is shown by this stoichiometric equation:

$$MnO_2(\text{bulk}) + SO_2 \longrightarrow MnSO_4(\text{bulk}) \qquad (5)^{3,5)}$$

Both the amount of SO_2 absorbed by MnO_2 and A_S/A_M, measured for the catalysts used for the SO_2-absorption experiments for 30 min in Fig. 1, have been plotted in Fig. 6 as functions of the experimental temperature; the A_S/A_M values have been corrected by considering the fraction of MnO_2 converted to $MnSO_4$, which was estimated from the amounts of SO_2 absorbed by the catalyst at each temperature. The similarity between the shapes of the two curves supports the idea that the reaction between SO_2 and MnO_2 can be described by the stoichiometric Eq. 5.

The Role of the SO_4^{2-}-complex in Butene Isomerization. The cis-trans isomerization and the copolymerization have been carried out over catalysts on which SO_2 had been preabsorbed at various temperatures (20—350 °C) for 30 min under the same experimental conditions as those used in Fig. 1. The rate of the cis-trans isomerization, $R_{c\to t}$, and the relative concentration of the formed polysulfone, A_P/A_M, the optical density for the band at 1300 cm^{-1} due to the polysulfone[6] divided by that at 710 cm^{-1} due to Mn–O, have been plotted in Fig. 7 as functions of the temperature for the SO_2 absorption. The circles and the triangles are the data obtained for the MnO_2 pretreated in a vacuum at 100 and 0 °C respectively. The dotted curve illustrates the relative amount of the SO_4^{2-}-complex (arbitrary unit), already shown in Fig. 6. The similar dependence on the absorption temperature between the rate of isomerization and the polysulfone formation illustrated in Fig. 7 can be explained by the fact that the latter reaction accompanies the former, as is demonstrated below:[6]

$$\textit{cis- or trans-}\text{2-butene} + \cdot SO_2[CH(CH_3)CH(CH_3)SO_2]_n$$
$$\rightleftharpoons \cdot CH(CH_3)CH(CH_3)\text{-}SO_2[CH(CH_3)CH(CH_3)SO_2]_n \qquad (6)$$

For the catalysts on which SO_2 has been preadsorbed at temperatures lower than 200 °C, the rate of the cis-trans isomerization increases in parallel with the increase in the amount of the SO_4^{2-}-complexes as the absorption temperature is raised. The catalyst outgassed at 0 °C shows a higher catalytic activity than that outgassed at 100 °C; this corresponds to the fact that the former catalyst demonstrates a higher concentration of SO_4^{2-}-complexes than the latter (Fig. 4). These results suggest that the catalytic activity of MnO_2 in the copolymerization, and accordingly for the cis-trans isomerization, is closely related to the formation of sulfate ions on the catalyst. The surface manganese must be positively charged by the

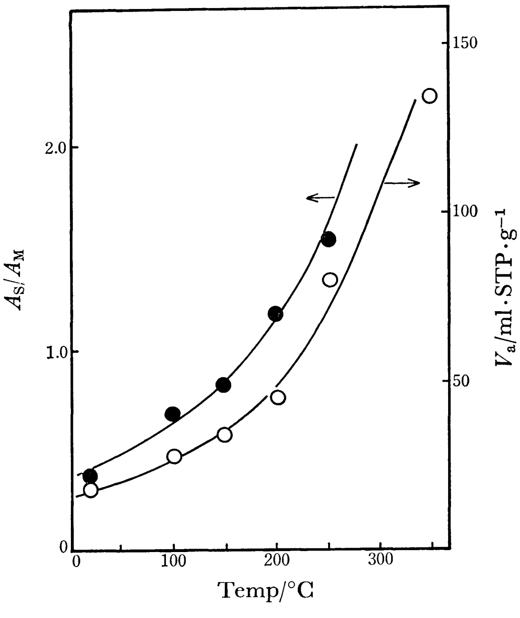


Fig. 6. Effect of temperature on the relative amount of SO_4^{2-} complex and the amount of SO_2 absorbed by MnO_2: (●); A_S/A_M, (○); V_a.

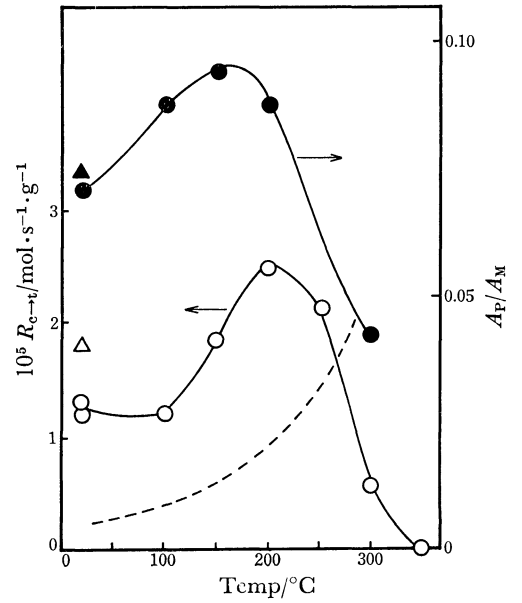
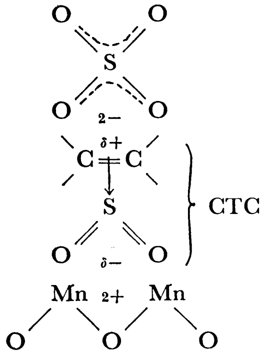


Fig. 7. The rate of isomerization, $R_{c\to t}$, and the amount of formed polysulfone, A_P/A_M, as a function of temperature for SO_2 absorption: circles; data for MnO_2 pretreated at 100 °C, triangles; data for MnO_2 pretreated at 0 °C. (●) and (▲); A_S/A_M, (○) and (△); $R_{c\to t}$. The dotted curve represents A_S/A_M (arbitrary unit) shown in Fig. 6.

formation of sulfate ions because of an electron transfer from the surface to the sulfate ions (Schemes 2—4), resulting in a generation of strong electrostatic fields on the surface. The picture of the initiation step for the reactions hypothesized previously,6,10) *i.e.*, a polarization of the charge-transfer complex (CTC) of SO_2 and butene under the influence of the electrostatic field on the surface, can also be adopted in the present work. The CTC positioned between the manganese cation and the sulfate anion on the surface may be strongly polarized and activated by a concerted action of the anion-cation pairs, as is illustrated below:



(7)

The catalytic activities of MnO_2 on which SO_2 has been preabsorbed at high temperatures ($> \approx 200$ °C) decrease, however, as the SO_2-treatment temperature is raised (Fig. 7). The catalytic activity of pure $MnSO_4$, pretreated in the presence of SO_2 at 200 °C, has been tested for the cis-trans isomerization. The activity per unit of surface area was less than 1/15 of that for MnO_2, which was tested under the same experimental conditions, implying that the decrease in the activity of MnO_2 pretreated with SO_2 at the high temperatures might result from a considerable transformation of MnO_2 to $MnSO_4$ deep into the bulk of MnO_2; eventually, then, the character of the surface becomes quite close to that of pure $MnSO_4$. The low catalytic activity of $MnSO_4$ can be attributed to a low affinity of its surface to the adsorption of SO_2 and, consequently, to a low concentration of CTC, which is necessary for the two reactions.

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