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The Isomerization of *cis*-2-Butene over SO_2-adsorbing $Mg(OH)_2$ and MgO

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The reaction of butenes caused by the surface compounds formed from SO_2 on $Mg(OH)_2$ or MgO has been studied. It has been shown that the cis-trans isomerization of 2-butene is selectively induced by the sulfur compounds. This specific isomerization has been explained by the previously proposed mechanism that the reaction is accompanied by the copolymerization of 2-butene and SO_2. The infrared spectroscopic study on the sulfur compounds formed on $Mg(OH)_2$ or on MgO has demonstrated the presence of SO_3^{2-}, SO_4^{2-}, or sulfinato complexes. The formation of these surface species may cause a strong electrostatic field on the surface, resulting in the polarization of reactant molecules, which is necessary for the initiation of the copolymerization or of the cis-trans isomerization. It has been shown, however, that the presence of weakly adsorbed SO_2 is essential for determining the catalytic activities of the solids in the SO_2-induced isomerization.

The need to understand gas-aerosol reactions in the atmosphere stems from the potential impact of such reactions on atmospheric chemistry, as well as their contribution to atmospheric haze formation and health effects attributable to aerosols in the respirable size range. Heterogeneous reactions of SO_2 and the contribution of the reactions to atmospheric sulfate aerosol are considered to be important to the over all pollution problem.[1–4] There are many reports which relate to the reactions between SO_2 and various solid particulates likely to be found in the polluted atmosphere.[5–12] However, very little is known about the possible, thermal reactions of SO_2 with hydrocarbons over solid particulates.

Preliminary experiments showed that the addition of SO_2 onto such solids as SiO_2, Al_2O_3, Fe_2O_3, CaO, $Ca(OH)_2$, MgO, or $Mg(OH)_2$, all of which are likely to be found in urban aerosols, causes the isomerization of butene. The most active solids to the reaction were MgO and $Mg(OH)_2$. Hence, we intend to report here the reaction over $Mg(OH)_2$ and MgO in the presence of the sulfur compounds on their surfaces formed from SO_2, which were confirmed by infrared spectroscopic measurement. The reaction mechanism and the nature of the active sites will also be discussed.

Experimental

Materials. The $Mg(OH)_2$ used in these experiments was reagent-grade powder from the Kanto Chemical Co., Inc. The reagent SO_2 gas, of anhydrous grade and supplied by the Matheson Chemical Co., and *cis*-2-butene gas, a high-purity product of the Phillips Petroleum Co., were purified by the freeze-pump technique.

Procedure. In the infrared spectroscopic experiments, a self-supporting $Mg(OH)_2$ wafer was made by pressing powder (about 15 mg) in 2-cm-diameter stainless steel discs at 2.7 t/cm^2. The wafer was then placed into the IR-cell for pretreatment and spectroscopic measurements. The sample wafer was degassed in a vacuum with increasing temperature to a required value between 100 and 600 °C. The rate of heating was 10 °C/min. Evacuation was further kept at the fixed temperature for 2 h. After the base-line spectrum of the wafer had been recorded at 20 °C, a known amount of SO_2 was adsorbed onto the wafer at the same temperature. Then the wafer was degassed in a vacuum for 3 min through a cold trap immersed in liquid nitrogen. After these procedures, the spectra of the sulfur compounds on the wafer were recorded. The amount of SO_2 remaining on the solid was calculated by the mass valance of the amount of SO_2 introduced and the amount of collected in a liquid nitrogen trap. A Shimadzu IR-430 grating spectrometer was used for all the infrared measurements.

The relative absorbance of the sulfur compounds, OD_s, on an unit surface area of the wafer was calculated by assuming the following, modified Lambert-Beer law equation,

$$OD_s = \left(\log \frac{I_0}{I}\right) \Big/ A = \varepsilon CW/A \qquad (1)$$

where I_0 represents the light intensity transmitted through the wafer of W in weight with a surface area of A (cm^2/g) in the absence of SO_2, I is the intensity of light transmitted through the wafer which contains the sulfur compounds of the concentration C (mol/g), and ε is the molar extinction coefficient.

The adsorption experiments were carried out volumetrically using a conventional closed system 119 cm^3 in volume. The BET surface area of the $Mg(OH)_2$ pretreated at different temperatures were determined by means of the nitrogen adsorption. The molecular cross sections of N_2 and SO_2 were taken as 16.2 and 19.2 Å^2 respectively.[13]

The isomerization of *cis*-2-butene in the presence or absence of SO_2 was carried out in a gas-circulation system with a volume of 210 cm^3. After the pretreatment of $Mg(OH)_2$ ($\approx$0.20 g), the reaction was started at 20 °C by feeding and circulating *cis*-2-butene gas at the pressure of 85 Torr, through the catalyst bed. A small amount of the reactant gas was periodically sampled and analyzed by gas chromatography. The initial rates of the isomerization were calculated from the concentration of the butene isomers formed in the initial 3 min. In the case of the SO_2-induced isomerization, a required amount of SO_2 was preadsorbed on the solid at 20 °C after the pretreatment of $Mg(OH)_2$. The solid was then evacuated slightly for 3 min before the addition of the reactant gas.

Results and Discussion

The State of the Catalyst after the Pretreatment. The state of the $Mg(OH)_2$ after evacuation pretreatment for 3 h at different temperatures has been examined by X-ray analysis. The results are summarized in Table 1, together with the surface areas of the samples. The

Table 1. The form of the solid and the BET surface area after the pretreatment

Pretreatment temperature/°C	Surface area $m^2\ g^{-1}$	The form of solid from X-ray analysis
100	21.4	$Mg(OH)_2$
200	27.4	$Mg(OH)_2$
300	295.0	MgO
400	282.0	MgO
500	251.0	MgO
600	221.0	MgO

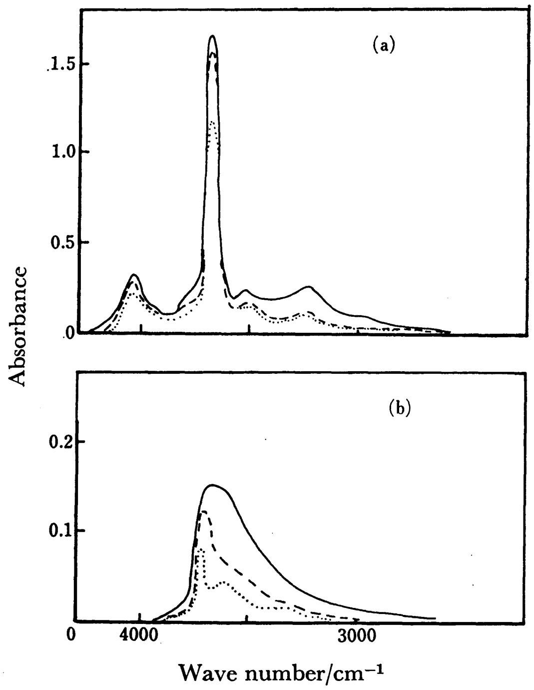

Fig. 1. Infrared spectra of hydroxyl groups for the samples pretreated at different temperatures.
The pretreatment temperatures: (a) —100 °C, ---200 °C, ···300 °C, (b) —400 °C, ---500 °C, ···600 °C.

X-ray data have shown that the $Mg(OH)_2$ dehydrated at the temperatures higher than 300 °C were converted into MgO face-centered cubic crystals. The surface areas were also drastically changed above 300 °C. Figure 1 shows the infrared spectra for the sample wafers in the wave number range of the stretching bands of hydroxyl groups. Only a slight decrease in the intensities of the hydroxyl bands was observed when the pretreatment temperature was increased from 200 to 300 °C, as is indicated in Fig. 1-a. These facts from the X-ray and infrared data imply that, under the dehydration conditions at 300 °C, only a part of the individual $Mg(OH)_2$ grains has been converted to MgO, while the $Mg(OH)_2$ grains are covered by MgO layers at the surface. The information from the X-ray analysis is limited to these surface MgO layers. A decrease in the intensity of hydroxyl groups is obvious at temperatures higher than 400 °C, suggesting that a further dehydration progresses into bulk $Mg(OH)_2$.

The SO_2-induced Cis-Trans Isomerization of cis-*2-Butene.* The catalytic activity of $Mg(OH)_2$ at 20 °C for the isomerization of *cis*-2-butene emerged when the sample was pretreated at temperatures above ≈400 °C. The steep increase in the catalytic activity as raising the activation temperatures above ≈400 °C is a general observation for the isomerization of olefin catalyzed by MgO[14—16] or CaO.[15,16] The catalytically active centers for the reaction, presumably the strongly basic O^{2-} ions, are considered to be created as a result of the removal of H_2O and/or CO_2 as raising the pretreatment temperatures for the catalysts.[14—16]

For the $Mg(OH)_2$ pretreated at the temperatures lower than 400 °C, the addition of SO_2 onto the surface induced the cis-trans isomerization of *cis*-2-butene without causing any double-bond migration to 1-butene. The absence of the double-bond migration has been confirmed using 1-butene as the starting olefin. The addition of SO_2 to the MgO prepared from $Mg(OH)_2$ by dehydration at 500 and 600 °C rather retarded the two isomerizations which proceeded with an appreciable rate in the absence of SO_2. The addition of SO_2 (5.4×10^{-10} mol/cm^2) to a sample pretreated at 600 °C stopped the progress of both the isomerizations. Further addition of SO_2, however, enhanced the rate of cis-trans isomerization selectively.

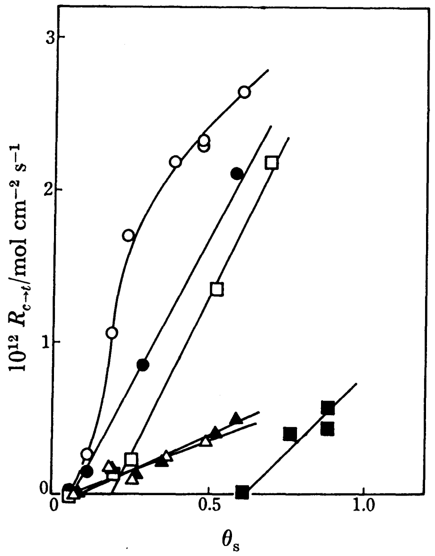

Fig. 2. The rate of SO_2-induced isomerization as a function of θ_s. The samples were pretreated at the following temperatures; (▲) 100 °C, (△) 200 °C, (●) 300 °C, (○) 400 °C, (□) 500 °C, (■) 600 °C.

The rates of SO_2-induced cis-trans isomerization on the catalysts pretreated at 100—600 °C have been plotted in Fig. 2 as a function of the apparent surface coverage of SO_2, θ_s.[17] The specific isomerization did not proceed until a critical amount of SO_2 had been preadsorbed. These values in θ_s are ≈0.1, ≈0.2, and ≈0.6 for the samples pretreated at 100—400 °C, at 500 °C, and at 600 °C, respectively. Beyond the critical θ_s, the rates of the reaction increased sharply.

The temperature effects on the rates of the SO_2-induced isomerization for the samples activated at 100 and 400 °C have been examined under the initial pressures of 85 and 49 Torr for *cis*-2-butene and SO_2 respectively. For both samples, the rates increased as the reaction temperatures were raised until 25 °C, but decreased above this temperature. The addition of a small amount of NO (less than 10% of the amount of SO_2) strongly inhibited the cis-trans conversion. These results suggest that the reaction proceeds by means of the polysulfone-accompanying mechanism proposed previously:[18–20]

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

The specific cis-trans isomerization proceeds *via* the addition and elimination of 2-butene molecules at the terminal of the polymer formed in the adsorption layer. The attempt to confirm the polysulfone production at 20 °C by infrared spectroscopic measurement was unsuccessful because the ceiling temperature for the copolymerization lies at about 25 °C.[19] The formation has, however, been confirmed using MgO in the reaction at −10 °C under 280 Torr of the *cis*-2-butene and SO_2 (1 : 1) gas mixture. The infrared spectra of the water of this sample have exhibited the two characteristic absorption bands ascribed to the polysulfone from *cis*-2-butene, one at 1300 cm^{-1} and the other at 1105—1140 cm^{-1}, attributable to the symmetrical and asymmetrical stretching vibrations of the sulfone groups respectively.[21]

Surface Sulfur Compounds from SO_2. Figure 3 shows the infrared spectra of the sulfur compounds on the samples pretreated at 100—600 °C, where OD_s was calculated by means of Eq. 1. At least eleven bands are apparent in the (b)-spectrum of Fig. 3. As the pretreatment temperature is raised from 300 to 600 °C, these resolved bands are diminished, but at least three broad bands, at 1030, 950, and 800 cm^{-1} are observed.

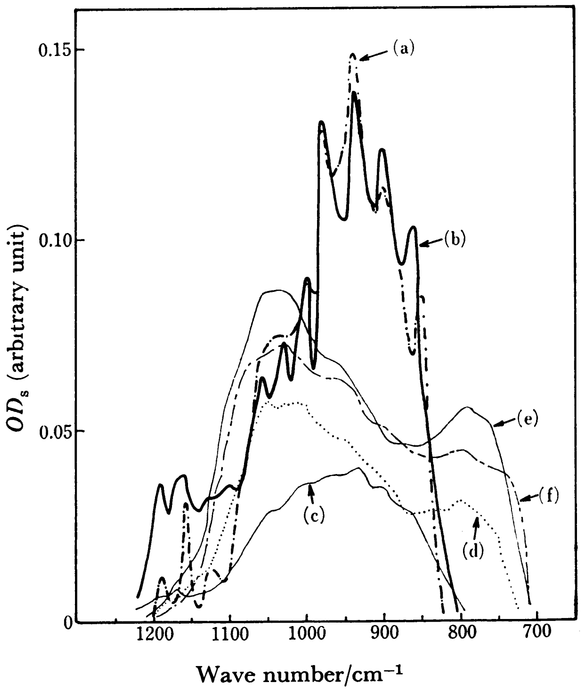

Fig. 3. The infrared spectra of the surface sulfur compounds on the samples pretreated at 100—600 °C. (a) Pretreatment temperature (T_p) 100 °C, θ_s=0.26, (b) T_p 200 °C, θ_s=0.26, (c) T_p 300 °C, θ_s=0.23, (d) T_p 400 °C, θ_s=0.17, (e) T_p 500 °C, θ_s=0.17, (f) T_p 600 °C, θ_s=0.19. SO_2-preadsorption at 20 °C.

Some bands from $Mg(OH)_2$ can be identified with reference to the work on MgO.[6,8] Schoonheydt and Lunsford have observed two different SO_3^{2-} species on MgO pretreated at 500 °C, one is an unidentate sulfito complex coordinated through an oxygen atom and the other a bidentate sulfito complex coordinated through its sulfur and oxygen atoms.[8] The former has absorption bands at 895, 925, and 975 cm^{-1}, and the latter, at 975, 1040, and 1070 cm^{-1}. The frequencies of the pair bands at 900, 940, and 980 cm^{-1} and those at 980, 1030, and 1060 cm^{-1} for the (a)- and (b)-spectra agree reasonably well with those of the pair bands observed by Schoonheydt and Lunsford. Thus, the bands between 900—1100 cm^{-1} in the (a)- and (b)-spectra can be assigned to the SO_3^{2-} species.

SO_3 species, including the sulfito complex, free SO_3^{2-} ions and free SO_3, do not exhibit absorption bands in 1100—1200 cm^{-1} region. The bands observed at this region and at 850—860 and 1000 cm^{-1} for Spectrum(a) or (b) may be ascribed to the formation of various SO_4^{2-} species which have been proposed by Goodsel *et al.*[6] and by Schoonheydt and Lunsford,[8] on MgO. Although the exact assignment of these surface sulfato complexes on $Mg(OH)_2$ cannot be verified from our experiments, the production of the SO_4^{2-} species at room temperature is a surprising observation, since the higher temperatures than 500 °C are usually needed for the formation of SO_4^{2-} species on alkaline earth metal oxides.[5,6,8]

In the case of the samples evacuated at high temperatures (>400 °C) (MgO), the broad bands between 700—1200 cm^{-1} do not allow the identification of the possible sulfur compounds. Schoonheydts and Lunsford speculated that SO_2 is present in the form of a sulfinato complexes on MgO at room temperature.[8] Goodsel and coworkers suggested the formation of unidentate- and bidentate-like sulfito complexes on the surface.[6] The broad bands in the (c)—(f) spectra may be attributed to these surface complexes.

Drastic changes in the spectra such as was shown in Fig. 3 when the pretreatment temperature was increased from 200 to 300 °C imply that the surface reactive species responsible for the SO_2—surface reactions may change in their nature between $Mg(OH)_2$ and MgO. Electron-donor centers associated with OH^- groups for $Mg(OH)_2$ or strongly basic O^{2-} ions for MgO may be necessary for the generation of the surface sulfur complexes described above.[14,22] The poisoning effect of SO_2 at low θ_s on the butene isomerizations observed on the samples activated at 500 and 600 °C can be ascribed to the consumption of the active centers, *i.e.*, the basic O^{2-} ions, by SO_2, producing sulfinato or SO_3^{2-} species.

Contribution of the Weakly Adsorbed SO_2 to the Isomerization of cis-*2-Butene.* It has been suggested that the polysulfone-accompanying cis-trans isomerization of 2-butenes (Eq. 2) is initiated through the strong polarization of the butene–SO_2 charge-transfer complexes under the influence of the electrostatic field on the catalyst surface.[19,20] The charge-transfer complex necessary for the reaction is formed from the butene and SO_2 molecules physisorbed. Therefore, knowledge about the sulfur compound remaining on the surface in the form of SO_2 is required to explain the peculiar feature of the reaction rates as a function of θ_s as is indicated in Fig. 2.

Goodsel *et al.* have observed the bands due to chemisorbed SO_2 on MgO at 1140 (ν_1) and 1322 cm^{-1} (ν_2), and those of the physisorbed SO_2 at 1149 and 1336 cm^{-1}.[6] In the present work the bands at 1140 and 1330 cm^{-1} becomes observable when θ_s increases beyond 0.50 in the case of the samples pretreated at 500 and 600 °C. For the samples pretreated at the temperature below 400 °C, the bands due to adsorbed SO_2, however, were not detected, probably because the weak band around 1140 cm^{-1} was hidden in the bands of SO_4^{2-} species and the band around 1330 cm^{-1} was obscured by the broad, strong band at 1290—1340 cm^{-1} attributable to carbonated species contained in $Mg(OH)_2$ as an unavoidable impurity.

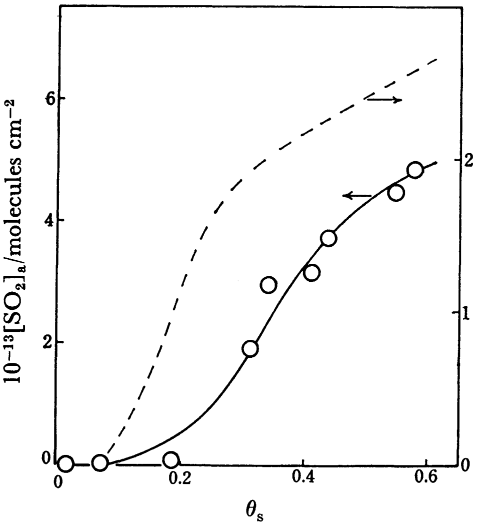

Fig. 5. The amount of weakly adsorbed SO_2 and the rate of isomerization of *cis*-2-butene over MgO as a function of θ_s: The sample was activated at 400 °C. —; The amount of weakly adsorbed SO_2, ---; the rate of cis-trans isomerization.

Since the information about the sulfur compound in the form of SO_2 derived from infrared spectroscopic experiments was scarce, a volumetric study has been carried out. The amount of SO_2 desorbed at 50 °C in 30 min from a surface with a fixed value of θ_s was measured by collecting the desorbed SO_2 by cold trap at 77 K. The amount of the weakly adsorbed SO_2 thus measured, $[SO_2]_a$, has been plotted as a function of θ_s in Figs. 4 and 5 for the samples activated at 100 and 400 °C respectively. The rates of the SO_2-induced isomerization of *cis*-2-butene are also shown by dotted curves in the figures. It is noticeable that the reaction rate and the amount of the weakly adsorbed SO_2 depend on θ_s in very similar ways. The correlation between the rate of the SO_2-induced isomerization and the amount of weakly adsorbed SO_2 has been examined at the fixed θ_s of 0.57. The results are shown in Figs. 6 and 7 for $Mg(OH)_2$ and MgO respectively. Here also a good correlation between the rate and the amount of weakly adsorbed SO_2 has been demonstrated.

The ratios of the amount of weakly adsorbed SO_2 to that of the total sulfur compounds at θ_s of 0.57, on the basis of the sulfur atoms, are 0.25 and 0.015 for the samples pretreated at 100 and 600 °C respectively. Most of the sulfur compounds remaining on the surface after desorption treatment must be in the form of the SO_3^{2-}, SO_4^{2-}, or sulfinato complexes described previously. At a low θ_s the added SO_2 must have been converted to these sulfur compounds as a result of the reaction with the solid, leaving no physisorbed SO_2 necessary for the specific isomerization. The absence

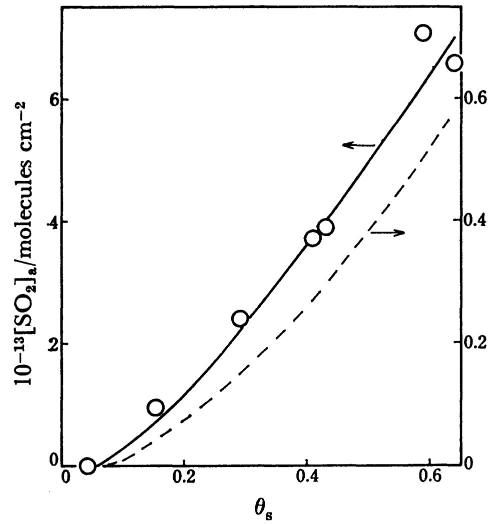

Fig. 4. The amount of weakly adsorbed SO_2 and the rate of cis-trans isomerization of *cis*-2-butene on $Mg(OH)_2$, as a function of θ_s: The sample was activated at 100 °C. —; The amount of weakly adsorbed SO_2, ---; the rate of cis-trans isomerization.

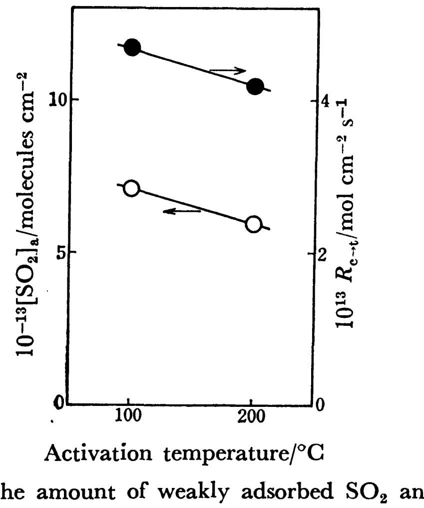

Fig. 6. The amount of weakly adsorbed SO_2 and the rate of isomerization of *cis*-2-butene on $Mg(OH)_2$ as a function of pretreatment temperatures: (●); the rate of cis-trans isomerization, (○); the amount of weakly adsorbed SO_2. θ_s=0.57.

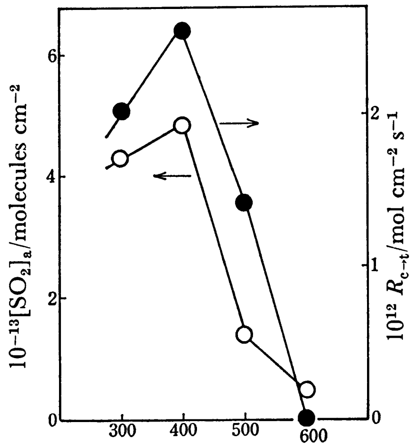

Fig. 7. The amount of weakly adsorbed SO_2 and the rate of isomerization of *cis*-2-butene on MgO as a function of pretreatment temperatures: (●); The rate of cis-trans isomerization, (○); the amount of weakly adsorbed SO_2. $\theta_s=0.57$.

of the reaction at the θ_s less than the critical values shown in Fig. 2 can be ascribed to the absence of the weakly adsorbed SO_2, as has been described above.

The amount of *cis*-2-butene adsorbed per unit of the surface area did not change with the θ_s for the samples activated at 100—600 °C; for example, it was $20.0\pm 1.2\times 10^{13}$ molecules/cm^2 for the samples activated at 300—600 °C over the range of θ_s of 0.05—0.60. Therefore, the change in the rate of the cis-trans isomerization shown in Figs. 2, 6, and 7 cannot be ascribed to that in the amount of the adsorbed *cis*-2-butene. A good correlation between the isomerization rate and the amount of weakly adsorbed SO_2 (Figs. 4—7) indicates that the activities of the solids for the polysulfone-accompanying isomerization are determined by the concentration of the weakly adsorbed SO_2 remaining on the surface.

The picture of the initiation step of the copolymerization, and accordingly of the cis-trans isomerization, that we have in mind is the polarization of the SO_2–butene charge-transfer complex under the influence of electrostatic field due to exposed surface ions.[20] As a consequence of the formation of the SO_3^{2-}, SO_4^{2-} species or sulfinato complexes, the surface magnesium will be positively charged due to electron transfer from the surface to these ionic species, and a strong electrostatic field would be formed. The concerted action of the negatively charged sulfur complexes—magnesium cation pairs may promote the strong polarization of the charge-transfer complex, causing the initiation of the copolymerization.

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