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Preparation of Solid Catalysts for Vapor-Phase Decomposition of Carbonyl Sulfide

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The vapor-phase catalytic decomposition of COS ($COS \rightarrow CO+1/xS_x$ and $2COS \rightarrow CO_2+CS_2$) has been mechanistically investigated so as to prepare solid catalysts which are active and selective for the first reaction. The comparison of the catalytic activity and selectivity of a series of Al_2O_3 catalysts with their acid-base properties and the different behavior of these two catalytic decomposition reactions in the poisoning of an Al_2O_3 catalyst with SO_2 demonstrate that electron-donating sites catalyze the first reaction whereas Lewis acidic sites do so the second reaction. CaO catalysts are prepared by thermal decomposition of $CaCO_3$ at elevated temperatures and their catalytic activity is compared with their amount of electron-donating sites. The greatest catalytic activity and selectivity for the first reaction(yield of $CO+S_x$=21.4%, selectivity=80.2% at 873 K) are obtained over CaO catalyst prepared at 1123 K which has the greatest electron-donating ability. These values of the yield and selectivity to $CO+S_x$ are much greater than those obtained over Al_2O_3 catalysts.

The catalytic decomposition of COS to CO and elemental sulfur is of industrial importance in view of the recovery of hydrogen from H_2S and the oxidative dehydrogenation of hydrocarbons.

Fukuda and co-workers[1)] proposed the following two-step closed cycle for the decomposition of H_2S.

$$H_2S + CO \longrightarrow H_2 + COS \tag{1}$$

$$COS \longrightarrow CO + 1/xS_x \qquad (x=2,4,6,\cdots) \tag{2}$$

They reported that almost an equilibrium conversion of H_2 could be produced in the first reaction at 493—573 K with a cobalt sulfide catalyst.[2)] In the second reaction, however, both CO_2 and CS_2 were always produced by the side reaction (Reaction 3) and in the case of homogeneous decomposition reaction such an elevated temperature as 1103 K had to be used for the decomposition of COS to CO and elemental sulfur (S_x) with a selectivity of 95%.[2)]

$$2COS \longrightarrow CO_2 + CS_2 \tag{3}$$

On the other hand, COS has been employed as a source of atomic sulfur in the catalytic oxidative dehydrogenation of lower paraffinic hydrocarbons and arylalkyl compounds.[3—6)] In this oxidative dehydrogenation, COS is catalytically decomposed to CO and atomic sulfur which then abstracts hydrogen atoms from these hydrocarbons to give unsaturated hydrocarbons and H_2S. The most striking feature of this dehydrogenation is the ability to produce unsaturated hydrocarbons with high selectivity even over such catalysts SiO_2, Al_2O_3, MgO, and TiO_2 as have conventionally been used as carriers.

Although the catalytic decomposition of COS is thus industrially important, only a few papers have been published on the mechanism of the catalytic reaction and the preparation of active and selective catalysts.[5,7)] In the present work, we have elucidated the nature of surface active sites responsible for the second and third reactions and have then tried to prepare active and selective catalysts for the second reaction by thermal decomposition of $CaCO_3$.

Experimental

Reaction and Catalyst. Vapor-phase catalytic decomposition of COS was carried out using a conventional flow fixed-bed reactor at atmospheric pressure (1 Torr=133.322 Pa). The reactor system comprised a 15-mm-i.d. quartz tube, 400 mm long, and a concentric thermowell. The reactor was heated with a cylindrical electric furnace. The catalysts employed are the referenced Al_2O_3 catalysts of the Catalysis Society of Japan (JRC-ALO-1, -2, -4, and -5) and CaO. CaO catalysts were prepared by thermal decomposition of $CaCO_3$ (Mallincrodt Inc., 99.95% purity) at elevated temperatures. Raschig rings (2×2 mm) were added above and below the catalyst bed. Purchased COS of greater than 97.5 vol% purity (Matheson Co., CO_2 1.4 vol%, N_2+CO 0.6 vol%, CS_2 0.19 vol%, O_2 0.10 vol%, and H_2O 0.01 vol%) was used without further purification. For convenience, helium (purity>99.99 vol%) was used as the diluent in the catalytic studies, and the total feed rate was always held at 200(NTP) $cm^3\,min^{-1}$: the standard feed composition of COS was 5.0 vol%.

Analysis. The reaction products (COS, CO, CO_2, and CS_2) were analyzed by gas chromatography using Porapak R(0.8 m, 363 K) and Porapak S(0.6 m, 363 K) in series as the separating column and helium as the carrier gas. The ESR measurements were carried out with a JEOL JES-PE spectrometer operating in the X band, adopting a 100 kHz modulation frequency. The g values of paramagnetic species were determined by the use of Mn^{2+} dissolved in MgO, and radical concentrations were estimated by comparing with the standard solution of 2,2-diphenyl-1-picrylhydrazyl in benzene. Purchased SO_2 (Matheson Co., purity>99.98%) was used in the ESR studies after purification by freeze-pumping method.

Results

Nature of Active Sites. Table 1 summarizes the results of catalytic decomposition of COS at 873 K over the referenced Al_2O_3 catalysts of the Catalysis Society of Japan. Previous experiments indicated no effects of film and pore diffusions on the catalytic activity and selectivity in the decomposition of COS at 873 K (catalyst size=10—100 mesh, pore diameter=84—309 Å). Previous experiments also indicated the ratio of the yield of CO_2 to that of CS_2 to be unity in the catalytic decomposition of COS up to 923 K, and no significant change in the catalytic activity and selectivity with time was observed at 473—923 K. The yield of $CO+S_x$ was 14.3% over JRC-ALO-2 Al_2O_3, but it increased gradually with increasing the amount of basic sites and reached 16.9% over JRC-ALO-5 Al_2O_3. The selectivity to $CO+S_x$ also increased from 25.7% to 36.0% with such a change in the chemical properties of Al_2O_3 catalysts. In contrast, the yield of CO_2+CS_2 was the greatest, 41.3%, over the most acidic Al_2O_3 catalyst (JRC-ALO-2) and the selectivity to $CO+S_x$ was the lowest, 25.7%, over this catalyst.

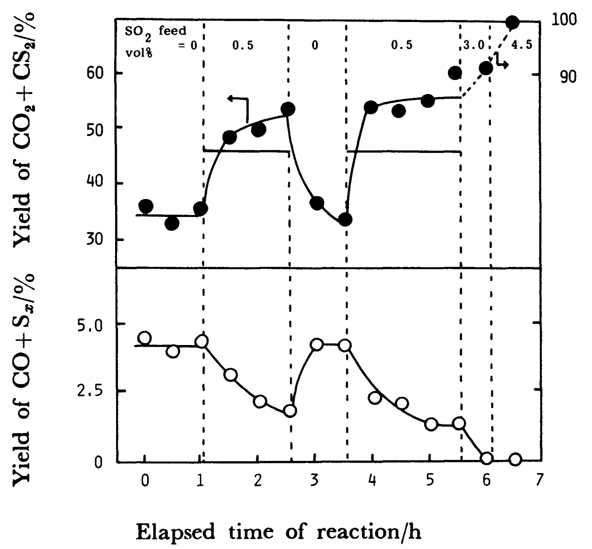


Fig. 1. Poisoning and promotional effects of SO_2 on the catalytic decomposition of COS at 763 K. Catalyst: JRC-ALO-4 Al_2O_3 1.0 g. COS+He: 200 (NTP)cm^3 min^{-1} (COS 10.0 vol%). The horizontal solid lines show the sum of the yield of CO_2+CS_2 in the absence of SO_2 (ca. 36%) and the yield of CO_2 calculated by assuming the complete consumption of introduced SO_2 due to Reaction 4(10.0%).

The participation of electron-donating sites and acidic sites in the catalytic decomposition of COS was confirmed by the poisoning of JRC-ALO-4 Al_2O_3 catalyst with SO_2 at 763 K (Fig. 1). That is, the yield of $CO+S_x$ over JRC-ALO-4 Al_2O_3 decreased from 4.3% to 1.7% upon introduction of SO_2 into the reactant mixture (0.5 vol%) and the yield was nearly 0% when the concentration of SO_2 in the feed mixture was 3.0 and 4.5 vol%. When JRC-ALO-4 Al_2O_3 was degassed at 773 K for 1 h and then exposed to 20 Torr SO_2 at 673 K for 30 min, SO_2^- radicals with g values of $g_\perp=2.002$ and $g_{/\!/}=2.008$[9] were formed with an amount of ca. 10^{17} spins g^{-1}.

In contrast, the yield of CO_2+CS_2 increased upon introduction of SO_2 (Fig. 1). Here, a portion of SO_2 introduced reacted with COS to produce CO_2 and elemental sulfur according to Reaction 4.

$$SO_2 + 2COS \longrightarrow 2CO_2 + 3/xS_x \tag{4}$$

However, the yields of CO_2 observed in the presence of SO_2 were always greater than the sum (ca. 46%) of the yield of CO_2+CS_2 observed in the absence of SO_2 (ca. 36%) and that of CO_2 calculated by assuming the complete consumption of introduced SO_2 due to Reaction 4 (10.0%) (Fig. 1). This result is an evidence for the view that participation of acidic sites in the catalytic decomposition of COS to CO_2+CS_2 took place, as discussed later in this paper.

Preparation of CaO Catalysts. The results of Table 1 and Fig. 1 suggest that strongly basic and less acidic catalysts are superior for the catalytic decomposition of COS to $CO+S_x$. The preparation of

Table 1. Results of the Decomposition of COS over Al_2O_3 Catalysts at 873 K

Al_2O_3 catalysts	JRC-ALO-2	JRC-ALO-1	JRC-ALO-4	JRC-ALO-5
BET surface area/m^2 g^{-1}	298	176	174	253
Basic sites/10^{16} g^{-1}	3.42	3.52	3.89	4.43
Acidic sites/mmol g^{-1}	0.84	0.70	0.50	0.70
Conversion of COS/%	55.6	46.7	49.6	47.0
Yield of $CO+S_x$/%	14.3	15.6	16.7	16.9
Yield of CO_2+CS_2/%	41.3	31.1	32.9	30.1
Selectivity to $CO+S_x$/%	25.7	33.4	33.7	36.0

Catalyst: 1.0 g. COS+He:200(NTP) cm^3 min^{-1} (COS 5.0 vol%).
Data for the physicochemical properties of Al_2O_3 catalysts: Ref. 8.

strongly basic metal oxides by thermal decomposition of alkaline earth metal carbonates has been reported.[10] We have prepared CaO catalysts by thermal decomposition of $CaCO_3$ and then compared their catalytic activity and selectivity with their amount of electron-donating sites. Here, the amount of electron-donating sites was determined by the amount of SO_2^- radicals formed upon adsorption of SO_2 on CaO. Figure 2 shows the ESR spectrum of SO_2^- radicals formed on CaO. Figure 3 shows the variation of the amount of SO_2^- radicals formed on CaO prepared at different decomposition temperatures. $CaCO_3$ (0.178 g=CaO 0.10 g) was decomposed at various elevated temperatures for 5 h under 10^{-5} Torr. The obtained CaO was exposed to SO_2 at the pressure of 10 Torr at room temperature and was then heated at 473 K for 30 min in the presence of SO_2. The g values of SO_2^- radicals formed, g_1=2.008 and 2.009, g_2=2.004, and g_3=2.002 (Fig. 2), agree well with those reported.[10] The amount of SO_2^- radicals was negligibly small over CaO prepared at 873 K, but it increased with rising decomposition temperature to reach the maximum value (ca. 2×10^{17} spins g CaO^{-1}) at 1073—1123 K and then decreased with further rise (Fig. 3).

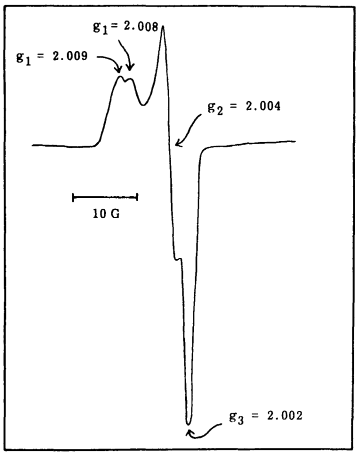


Fig. 2. ESR spectrum of SO_2^- radicals formed on CaO.
$CaCO_3$: 0.178 g (=CaO 0.10 g), decomposed at 1053 K for 5 h under 10^{-5} Torr. SO_2: 10 Torr, adsorbed at room temperature and then heated at 473 K for 30 min.

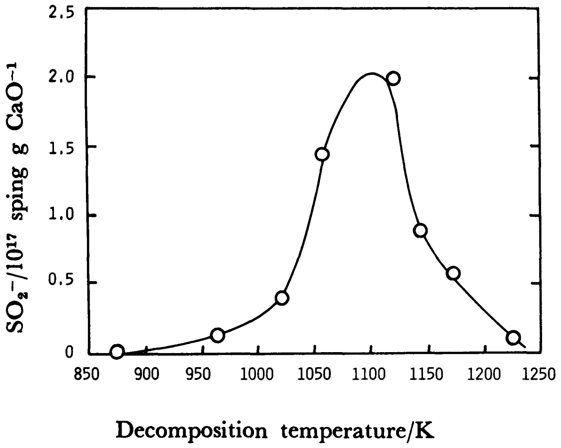


Fig. 3. Variation of the amount of SO_2^- radicals formed on CaO with rising decomposition temperature for thermal decomposition of $CaCO_3$.
$CaCO_3$: 0.178 g (=CaO 0.10 g), decomposed for 5 h under 10^{-5} Torr. The obtained CaO was exposed to SO_2 at the pressure of 10 Torr at room temperature and was then heated at 473 K for 30 min.

The rapid decrease in the amount of SO_2^- radicals above 1123 K is caused by the crystallization of CaO formed.[10] CaO catalyst prepared at a decomposition temperature of 1123 K had the greatest amount of electron-donating sites (Fig. 3).

Catalytic Decomposition of COS over CaO. Figure 4 shows the variation of the catalytic activity of CaO with rising decomposition temperature for $CaCO_3$. Here, $CaCO_3$ (0.89 g=CaO 0.50 g) was weighed into the catalytic reactor and was then decomposed for 5 h at various temperatures in flowing He(100(NTP) cm^3 min^{-1}). The obtained CaO was employed for catalytic studies without any exposure to air. These CaO catalysts also showed no significant change in the catalytic activity and selectivity with time during the decomposition of COS. The yield of CO+S_x over CaO prepared at 923 K was 19.7% at 873 K, but it increased gradually with rising decomposition temperature to reach the

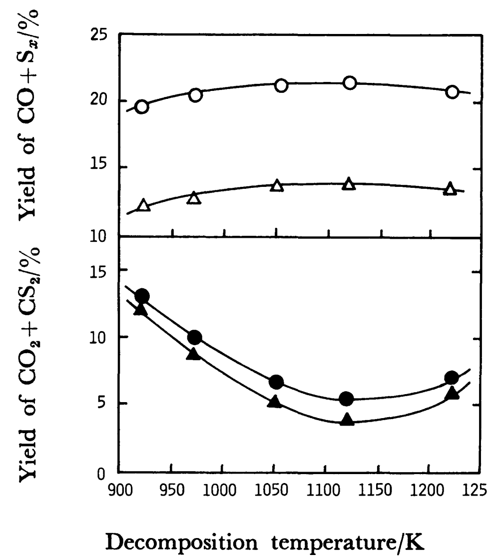


Fig. 4. Variation of the catalytic activity of CaO with rising decomposition temperature for $CaCO_3$. $CaCO_3$: 0.89 g (=CaO 0.50 g), decomposed for 5 h in flowing helium (100(NTP)cm^3 min^{-1}) in the catalytic reactor. COS+He: 200 (NTP)cm^3 min^{-1} (COS 5.0 vol%). Reaction temperature: △,▲ —823 K, ○,● —873 K.

maximum value (21.4%) at a decomposition temperature of 1123 K and then decreased with further rise in decomposition temperature (Fig. 4). On the other hand, the yield of CO_2+CS_2 over CaO prepared at 923 K was 12.9% at 873 K, but it decreased with rising decomposition temperature to reach the minimum value (5.3%) at 1123 K and then increased with further rise. The selectivity to CO+S_x at 873 K thus increased from 60.4% to 80.2% with rising decomposition temperature from 923 K to 1123 K and then decreased to 76.4% at 1223 K. A similar behavior of the catalytic activity and selectivity is seen at a reaction temperature of 823 K (Fig. 4). X-Ray diffraction analysis revealed no formation of calcium sulfide and calcium carbonate in these CaO catalysts during the catalytic decomposition of COS at 823 and 873 K. Thus, CaO catalyst prepared by thermal decomposition of $CaCO_3$ at 1123 K was the most active and selective one in the CaO prepared in the present work.

Effect of the Volume of Reactor. The observed relation of the yield of CO+S_x with the temperature for thermal decomposition of $CaCO_3$ is fairly flat and the catalytic activity of CaO for the second reaction does not change so sharply as the amount of SO_2^- radicals formed (Figs. 3 and 4). A similar behavior can be seen between the yield of CO+S_x over the referenced Al_2O_3 catalysts and their amount of basic sites (Table 1). These results suggest one possibility that a heterogeneously initiated homogeneous decomposition of COS to CO+S_x also took place in the catalytic decomposition of COS at 823—873 K. This additional decomposition reaction must be of chain-reaction type. We have also studied the effect of volume of the reactor below catalyst bed on the catalytic activity and selectivity of JRC-ALO-4 Al_2O_3 at 873 K. As summarized in Table 2, the yields of CO+S_x and CO_2+CS_2 and the selectivity to CO+S_x were 16.9, 32.4, and 34.2%, respectively, when the volume of reactor below catalyst bed was 10 cm^3. Nearly the same values were obtained for the volume of 35 cm^3 (Table 2). Thus, no effect of the volume on the catalytic activity and selectivity was found.

Table 2. Effect of the Volume of Reactor below Catalyst Bed on the Catalytic Decomposition of COS at 873 K

Volume/cm^3	10	35
Conversion of COS/%	49.3	49.5
Yield of CO+S_x/%	16.9	16.5
Yield of CO_2+CS_2/%	32.4	33.0
Selectivity to CO+S_x/%	34.2	33.3

Catalyst: JRC-ALO-4 Al_2O_3 1.0 g. COS+He: 200 (NTP) cm^3 min^{-1} (COS 5.0 vol%).

Discussion

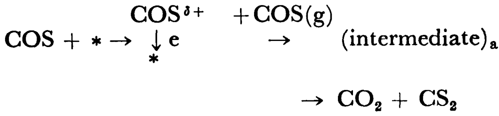
The mechanism of the vapor-phase catalytic decomposition of COS was first investigated by Haas and Khalafala.[7] Since the degree of decomposition at a given temperature was approximately the same for such diverse catalysts as α-Al_2O_3, χ-Al_2O_3, Ti/χ-Al_2O_3, and silica gel regardless of their BET surface area and chemical composition, the catalytic decomposition of COS was believed to take place thermocatalytically.[7] In our previous studies on the catalytic oxidative dehydrogenation of hydrocarbons with COS over SiO_2, Al_2O_3, MgO, and TiO_2, however, it was demonstrated that the catalytic activity of these metal oxides for the decomposition of COS to CO+S_x was great when the amount of electron-donating sites at the surface of these metal oxides was great.[6]

In the present work, the observed increase in the yield and selectivity to CO+S_x with increasing the basicity of Al_2O_3 catalysts (Table 1) suggests that the participation of electron-donating sites in the catalytic decomposition of COS to CO+S_x took place, as suggested previously.[6] On the other hand, the observation of the greatest yield of CO_2+CS_2 over the most acidic Al_2O_3 catalyst (JRC-ALO-2, Table 1) suggests the role of acidic sites (maybe Lewis acidic sites) in the catalytic decomposition of COS to CO_2+CS_2. These views are further supported by the results of poisoning of JRC-ALO-4 Al_2O_3 catalyst with SO_2 during the decomposition of COS, which resulted in the remarkable decrease in the yield of CO+S_x (Fig. 1). Since COS^- radicals formed on the surface of MgO were readily decomposed to CO+S_x even at low temperatures,[11] we believe that the catalytic decomposition of COS to CO+S_x took place through the donation of electrons from the catalyst surface to adsorbed COS molecules.

$$\mathrm{COS} + * \rightarrow \overset{\mathrm{COS}^{\delta-}}{\underset{*}{\uparrow}}\mathrm{e} \rightarrow \mathrm{CO} + \mathrm{S} \rightarrow \mathrm{CO} + 1/x\mathrm{S}_x, \tag{5}$$

where * is an electron-donating site at the surface of catalyst.

In contrast to the yield of CO+S_x, the yield of CO_2+CS_2 rather increased upon introduction of SO_2 (Fig. 1). It was reported that the catalytic activity of CaO–SiO_2 for the dehydrogenation of 1-butanol increased upon introduction of pyridine into the reactant mixture.[12] This promotional effect of pyridine was explained in terms of the high electron-donating ability of pyridine: The surface sites adjacent to adsorbed pyridines become rich in electron density and these sites act as basic sites.[12] In the present work, an acidic gas SO_2 was fed into the catalytic reactor and was adsorbed as SO_2^- at the surface of Al_2O_3 catalyst. Hence it is probable that upon introduction of SO_2 the strength of Lewis acidic sites adjacent to adsorbed SO_2^- was greatly enhanced or that the surface sites adjacent to adsorbed SO_2^- became acidic sites. We believe that this inductive effect of SO_2 gave rise to increase in the catalytic activity of Al_2O_3 for the decomposition of COS to CO_2+CS_2. A concerted mechanism involving the participation of Lewis acidic sites and electron-donating sites is rejected for the reaction of COS to CO_2+CS_2 since the latter sites were poisoned by SO_2 (Fig. 1). We now believe that a COS molecule adsorbed on a Lewis acidic site reacts with a gaseous COS molecule to form a surface intermediate which then decomposes into CO_2+CS_2.



$$\mathrm{COS} + * \rightarrow \begin{array}{c}\mathrm{COS}^{\delta+}\\ \downarrow e\\ *\end{array} + \mathrm{COS(g)} \rightarrow (\text{intermediate})_{\mathrm{ads}} \rightarrow \mathrm{CO_2} + \mathrm{CS_2} \qquad (6)$$

where * is a Lewis acidic site.

Haag and Miale[5] proposed that the catalytic decomposition of COS to CO_2+CS_2 takes place through participation of surface sulfur atoms evolved by the decomposition of COS to CO+S. In the present work, however, the catalytic decomposition of COS to CO_2+CS_2 took place even at such low reaction temperatures as 473—573 K at which the catalytic decomposition of COS to CO+S_x did not take place (e.g., JRC-ALO-2 Al_2O_3, yield of CO_2+CS_2= 17.8% at 473 K and 23.4% at 573 K). This finding does not support the mechanism of CO_2+CS_2 formation proposed by Haag and Miale. Thus, in addition to the thermocatalytic mechanism proposed by Haas and Khalafala,[7] we propose the mechanism for the decomposition of COS involving the participation of surface electron-donating sites and Lewis acidic sites.

The above mechanistic finding made in the present work indicates that strongly basic catalysts are superior for the selective decomposition of COS to CO+S_x. CaO catalysts prepared by thermal decomposition of $CaCO_3$ have been well known as strongly basic catalysts. In the present work, CaO catalysts thus prepared showed very low catalytic activities for the decomposition of COS to CO_2+CS_2 compared with Al_2O_3 catalysts and the selectivity to CO+S_x was as high as 60—80% at 873 K (Table 1, Fig. 4). Particularly CaO catalyst prepared at 1123 K, which had the greatest electron-donating ability, showed the greatest values of the yield and selectivity to CO+S_x (21.4 and 80.2%) and at the same time the lowest yield of CO_2+CS_2 (5.3%) at 873 K (Figs. 3 and 4). This superiority of CaO catalyst prepared at 1123 K can be understood by comparing with the equilibrium conversion of COS at 873 K. That is, in the reaction conditions empolyed in Table 1 and Fig. 4 elemental sulfurs at equilibrium are of S_2 type[13] and the equilibrium conversions of COS to CO+S_2 and CO_2+CS_2 are 27.3 and 35.3%, respectively, the selectivity to CO+S_2 being 43.6%.[14] Although the surface acidity was not determined for these CaO catalysts, the observation of the greatest values of the yield and selectivity to CO+S_x and the lowest value of the yield of CO_2+CS_2 over CaO catalyst prepared at 1123 K (Fig. 4) is as expected.

On the other hand, the absenece of the effect of volume of the reactor below catalyst bed on the catalytic activity and selectivity of JRC-ALO-4 Al_2O_3 (Table 2) does not indicate the presence of a heterogeneously initiated chain reaction-type homogeneous decomposition of COS to CO+S_x in the catalytic decomposition of COS. At present, the reason for the lack of a close relation between the yield of CO+S_x and the amount of SO_2^- radicals (Figs. 3 and 4) is not known. At any rate, the above findings made in the present work suggest the possibility that we can further enhance the catalytic activity and selectivity for the decomposition of COS to CO+S_x by preparing much more strongly basic catalysts.

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