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Photocatalyzed Isomerization of Butenes over Metal Sulfides. High Photocatalytic Activity and Its Origin

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Photocatalytic activity of CdS and ZnS for the *cis-trans* isomerization of 2-butene is much higher than that of TiO_2 and ZnO, though the double bond shift isomerization to 1-butene hardly proceeds in contrast with the case of the oxides. The addition of O_2 or NO molecules leads to the remarkable inhibition of photocatalyzed isomerization of 2-butene, but not to the complete inhibition. Water vapor enhanced the photocatalyzed isomerization. From these results together with the ESR measurements before and after UV irradiation of the sulfide catalyst either in the presence or in the absence of butene, the following conclusions emerge: sulfur radicals such as $\dot{S}_n$, which are produced by the hole trapping by lattice S^{2-} ions and/or sulfur clusters existing in the catalyst inherently, play a significant role in the weakening of the C=C double bond of 2-butene via the interaction with the molecules; the stability of such sulfur radicals results in the much higher photocatalytic activity of CdS and ZnS catalysts as compared with that of metal oxide catalysts.

Photocatalysis of powdered metal sulfides such as CdS and ZnS as well as the metal oxides has received much attention from the standpoint of photochemistry on solid surfaces as well as the potential possibility of utilization of solar energy. However, most studies have been mainly made with the reactions associated with the photodecomposition of water over semiconductors in the liquid-solid reaction system.[1,2] In order to clarify the true nature of the photocatalysis of the sulfides and oxides, it is necessary to investigate on a wide range of the photocatalyzed reactions, other than the oxidation and reduction reactions. Along this line, we have investigated the photocatalyzed isomerization of butenes over CdS and ZnS as well as over the oxides such as TiO_2 and ZnO in the gas-solid reaction system.[3-6]

Although a little attention has been paid on such photocatalyzed isomerization reactions,[3,7] more recently photocatalyzed isomerization reactions have been studied by a number of workers. De Mayo et al.[8] have reported that the *cis-trans* isomerization of substituted styrenes is photoinduced over CdS catalyst via the formation of radical cations from alkenes. Yanagida et al.[9] have reported that *cis-trans* isomerization of simple alkenes such as 2-octene is photoinduced by using CdS or ZnS powder as a photocatalyst and that photoformed hole centers at the surface play a significant role in the photocatalyzed isomerization in the liquid-solid reaction system.

As described previously, the double bond shift isomerization as well as *cis-trans* isomerization of 2-butene is markedly enhanced over the metal oxides such as TiO_2,[3-5] Ti-Si binary oxides,[6] and the highly dispersed supported metal oxides such as V_2O_5[10] under UV irradiation. Therefore, it is of special interest to investigate the photocatalyzed isomerization of butene molecules over the sulfides such as CdS and ZnS, and to compare their features with those observed over the metal oxides.[3-6] The present work deals with the photocatalyzed isomerization of 2-butene molecules over various kind of CdS and ZnS powdered catalysts in the gas-solid reaction system by means of ESR measurements of the photo-formed active species as well as analysis of the photo-formed reaction products.

Experimental

Butenes, O_2, and NO of pure grade were obtained from Takachiho Kagakukogyo Co. CdS and ZnS powders were obtained from Mitsuwa, Nakarai, Shimakyu, and Wako Chemicals Cos. CdS and ZnS catalysts were also prepared by the precipitation method from aqueous solutions of $CdCl_2$ or $ZnCl_2$ and Na_2S. Prior to the experiment, the catalyst was evacuated for one hour at 473 K for CdS and 573 K for ZnS, respectively. CdS (prepared by precipitation) which had been mixed mechanically with 5 wt% of sulfur powder (Nakarai) was also evacuated for one hour at 373 and 473 K, respectively. Butene of 4.0 kPa was introduced onto the catalyst which had been spread over the quartz window having a surface area of about 32 cm^2.

The photoisomerization was carried out by using a high pressure mercury lamp (Toshiba, SHL-100UV) without a filter in an ice-water bath. Gas samples were collected at definite time intervals and analyzed by a gas chromatography using a 2,4-dimethylsulfolane column. The photoisomerization of butene in the presence of O_2, NO, or H_2O vapor was also performed in the same experimental conditions as mentioned above. Quantum yields for the photoisomerization reactions were estimated by using the number of incident photons, the extinction coefficient of the catalyst, and the quantum yield of potassium trioxalatoferrate(III) actinometer at each excitation wavelength.

ESR measurements were carried out with a JES-ME-1 (X-band) spectrometer at 77 K. Mn^{2+} ions in MgO powder were used for g-values and sweep calibrations. UV irradiation for ESR measurements was carried out by using a 500 W mercury lamp with a color filter (Toshiba UV-29; $\lambda > 280$ nm) at 77 K.

Results

1. Photocatalyzed Isomerization of Butenes over CdS and ZnS Catalysts. As shown in Fig. 1, UV irradiation of ZnS in the presence of *cis*-2-butene molecules leads to the formation of *trans*-2-butene with high efficiency. However, the double bond shift isomerization toward 1-butene scarcely proceeds. Figure 2 shows the results of photocatalyzed isomerization of *cis*-2-butene over CdS catalyst at 273 K. The same feature that the isomerization proceeds mainly toward *trans*-2-butene was also obtained with CdS catalyst. The photocatalyzed isomerization of *trans*-2-butene over ZnS or CdS catalyst at 273 K was found to proceed toward *cis*-2-butene with little formation of 1-butene. Meanwhile, the photoisomerization of 1-butene toward 2-butene was not observed over the sulfide catalysts at 273 K. The isomerization of *cis*-2-butene in the dark conditions at 273 K over the sulfides scarcely proceeds, except for ZnS (Mitsuwa).

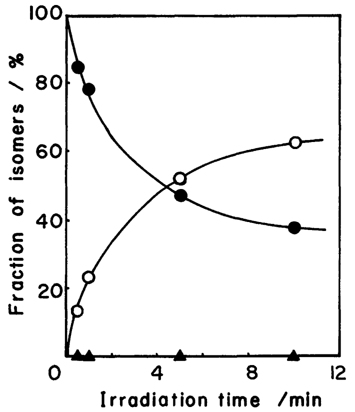


Fig. 1. Photocatalyzed isomerization of *cis*-2-butene over ZnS (prepared by precipitation) at 273 K. ●: *cis*-2-Butene, O: *trans*-2-butene, ▲: 1-butene. The light intensity was reduced to 9.8% of the original intensity by a screen.

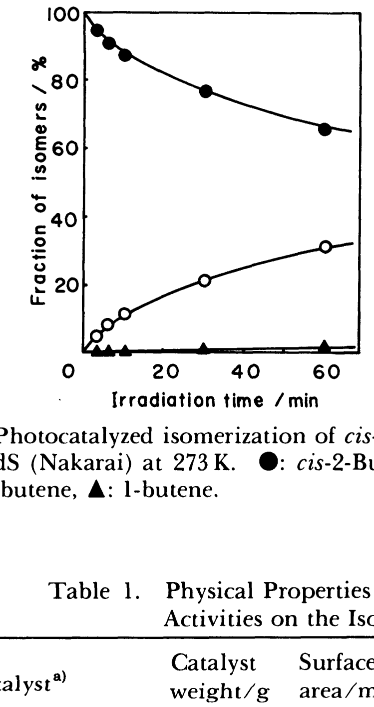


Fig. 2. Photocatalyzed isomerization of *cis*-2-butene over CdS (Nakarai) at 273 K. ●: *cis*-2-Butene, O: *trans*-2-butene, ▲: 1-butene.

The results of photoisomerization obtained with CdS and ZnS catalysts are summerized in Table 1, together with those obtained with TiO_2 and ZnO oxide catalysts.[3-5] It is generally found that the photocatalytic activity for the *cis*-*trans* isomerization of 2-butenes is much higher with the metal sulfide catalysts than with the metal oxide catalysts by about 2 or 3 orders of magnitude. However, the photocatalytic activity for the double bond shift isomerization of 2-butene is in the reverse relation, i.e., much lower with the sulfide catalysts than with the oxide catalysts. Table 1 also includes the various physical properties of the catalysts used in this work, i.e., BET surface area, crystal form, and band gap of the catalysts.

2. Effect of the Addition of O_2 or NO Molecules upon the Photoisomerization. The relative reaction rates for the isomerization of *cis*-2-butene toward *trans*-2-butene over CdS and ZnS are shown in Fig. 3 as a function of the added oxygen pressure. The addition of oxygen leads to the remarkable inhibition of photoisomerization of *cis*-2-butene, but not to the complete inhibition of the reaction. The photocatalyzed

Table 1. Physical Properties of Metal Oxide and Sulfide Catalysts and Photocatalytic Activities on the Isomerizations of *cis*-2-Butene over the Catalysts

Catalyst[a)]	Catalyst weight/g	Surface area/$m^2 g^{-1}$	Crystal form[b)]	Band gap[c)]/eV	Initial rate[d)]/nano mol s^{-1}		Apparent quantum yield[e)]
					cis→*trans*	*cis*→1	
TiO_2 (Degussa, P-25)	0.3	40[f)]	a(main)/r	2.95	4.8	8.29	2.3×10^{-5}
ZnO (Kadox 25)	0.6	10[f)]	h	3.10	1.0	0.87	3.2×10^{-6}
CdS (Nakarai, GR)	1.4	2.6[g)]	h	2.08	6.3	0.54	8.0×10^{-6}
CdS (Precipitation)	1.4	3.0[g)]	c	1.89	73.4	0.31	8.6×10^{-5}
ZnS (Mitsuwa, EL)	1.5	43.2[h)]	c	3.43	3040	0	5.1×10^{-3}
ZnS (Wako, CP)	1.5	7.0[h)]	c(main)/h	3.46	577	0.14	
ZnS (Shimakyu, CP)	1.5	14.4[h)]	c(main)/h	3.48	171	0.09	
ZnS (Nakarai, GR)	1.5	0.4[g)]	c	3.40	11.9	0.12	
ZnS (Precipitation)	1.5	83[g)]	c	3.33	1410	0.08	2.6×10^{-3}

a) The oxides were subjected to oxygen pretreatment for 1 h at 773 K followed by evacuation at the same temperature. The sulfides were pretreated by evacuating for 1 h at 473 K for CdS and at 573 K for ZnS. b) Observed by the X-ray diffraction. a, anatase; r, rutile; h, hexagonal; c, cubic. c) Determined from the absorption edge of UV reflection spectrum. d) The initial rate was evaluated by substracting the initial rate in the dark conditions from the initial rate under UV irradiation. The photoisomerization was carried out at 273 K, except for TiO_2 at 313 K. e) Sum total of both quantum yields for *trans*-2-butene and 1-butene. f) From Ref. 3. g) Determined by BET method. h) From Ref. 1.

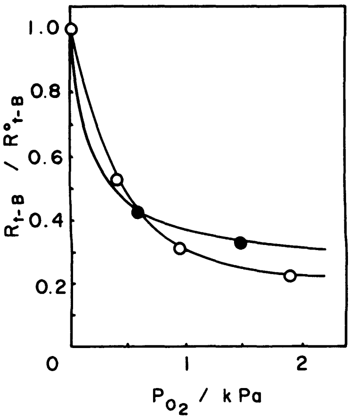


Fig. 3. Oxygen pressure dependences of the *trans*-2-butene yield on the photocatalyzed isomerization of *cis*-2-butene at 273 K over CdS (○) and ZnS (●) prepared by the precipitation method. $R_{t\text{-B}}/R^{\circ}_{t\text{-B}}$ denotes the ratio of the initial formation rate of *trans*-2-butene with oxygen to that without oxygen.

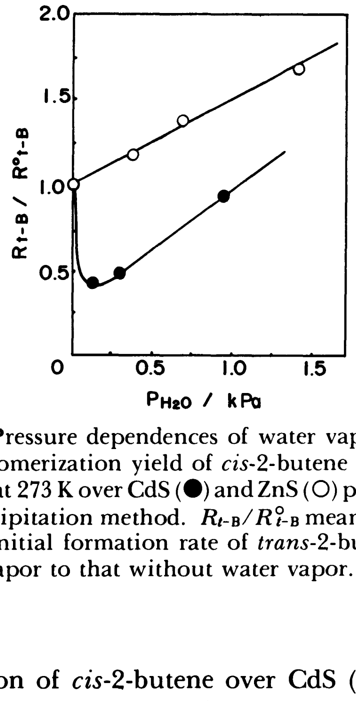


Fig. 4. Pressure dependences of water vapor on the photoisomerization yield of *cis*-2-butene to *trans*-2-butene at 273 K over CdS (●) and ZnS (○) prepared by the precipitation method. $R_{t\text{-B}}/R^{\circ}_{t\text{-B}}$ means the ratio of the initial formation rate of *trans*-2-butene with water vapor to that without water vapor.

isomerization of *cis*-2-butene over CdS (Nakarai) or ZnS (Mitsuwa) was also inhibited by the addition of NO in the same trend as the case for O_2.

3. Effect of Water Vapor on the Photocatalyzed Isomerization of *cis*-2-Butene. The effect of the added water vapor on the photocatalyzed isomerization has been investigated in order to obtain further informations about the feature of the reactions over the metal sulfides, since the details of the effect of adsorbed water on the photoisomerization over TiO_2 catalyst have been investigated[5] and it is well-known that water is an efficient photo-formed electron-trapping agent on H_2 evolution by ZnS photocatalyst in the liquid-solid system.[2] The relative reaction rates for the photocatalyzed isomerization of *cis*-2-butene over CdS and ZnS catalysts in the presence of water vapor are shown in Fig. 4. The relative rate with CdS increases with increasing the vapor pressure, though it decreases first in the very low pressure range. On the other hand, the rate of photocatalyzed isomerization of *cis*-2-butene with ZnS catalyst increases monotonously with increasing the pressure of water vapor. Thus, although the addition of water vapor onto the catalysts resulted in the enhancement of the photocatalyzed isomerization of *cis*-2-butene toward *trans*-2-butene, neither photohydrogenolysis nor photohydrogenation reactions to lead the formations of C_2H_6 and n-C_4H_{10}, respectively, were observed in these systems. Such results are a complete contrast to the features observed with the metal oxide catalysts[11] where the presence of adsorbed water has suppressed the photocatalytic isomerizations of *cis*-2-butene toward *trans*-2-butene and 1-butene and simultaneously enhanced the photohydogenolysis and photohydrogenation reactions.[5]

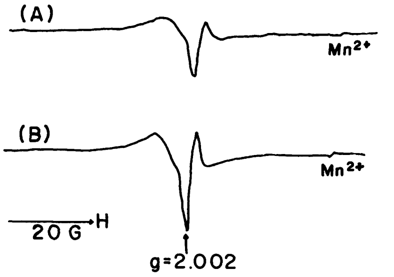


Fig. 5. ESR spectra of CdS (Nakarai) in the presence of *cis*-2-butene at 77 K. (A), before UV irradiation; (B), after UV irradiation. The catalyst was pretreated by evacuating for 1 h at 473 K.

4. ESR Measurements of the Catalysts. In order to obtain the informations about the photo-formed active species for the photocatalyzed isomerization reactions over the sulfides, ESR measurements were undertaken at 77 K. As shown in Fig. 5, the ESR spectrum having g-value of 2.002 is observed with CdS (Nakarai) in the dark conditions with *cis*-2-butene molecules (A state). The intensity of this ESR signal increases with UV irradiation of the catalyst with *cis*-2-butene at 77 K (B state). When it was again measured at 77 K after warmed up the B state at 77 K to room temperature in the dark conditions, the signal intensity decreased to the original level (A state).

As shown in Fig. 6, the similar features as the case for CdS are found with ZnS (Mitsuwa) catalyst, though ESR signal in this system seems to be more complicated. ESR signal having g-values of g_1=2.043, g_2=2.031, and g_3=2.003 is observed with the catalyst evacuated for one hour at 573 K (a state). The addition of *cis*-2-butene onto the catalyst led to a remarkable decrease of the signal intensity (b state). UV irradiation of the ZnS catalyst at 77 K in the presence of *cis*-2-butene leads to an increase of signal intensity with UV irradiation time (c state). When it was again measured at 77 K after warmed up the c state at 77 K to room temperature in the dark conditions (d state), the

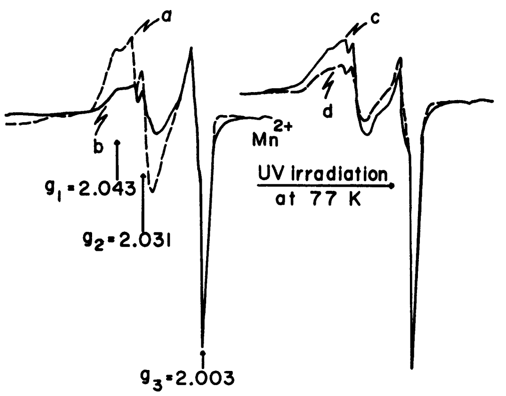


Fig. 6. ESR spectra for ZnS (Mitsuwa) at 77 K. a, in the absence of *cis*-2-butene; b, in the presence of *cis*-2-butene; c, irradiated in the presence of *cis*-2-butene; d, measured at 77 K after warmed up the c state at 77 K to room temperature in the dark conditions. The catalyst was pretreated by evacuating for 1 h at 573 K.

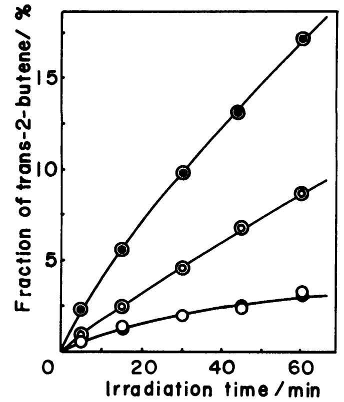


Fig. 7. Effect of the sulfur addition on the photocatalyzed isomerization of *cis*-2-butene over CdS (prepared by precipitation) at 273 K. Pretreatment temperature and existence of sulfur, ○: 373 K without sulfur, ●: 473 K without sulfur, ⊙: 373 K with sulfur of 5 wt %, ◎: 473 K with sulfur of 5 wt %.

signal intensity decreased to the revel of the original b state.

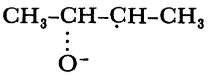
The effect upon the ESR signal of the addition of O_2 or NO molecules which led to inhibition of the photocatalyzed isomerization of 2-butene has been undertaken. The addition of oxygen or NO molecules onto the ZnS or CdS catalyst was found to reduce the ESR signal intensity without any appearance of new ESR signals even after UV irradiation of the catalysts at 77 K.

According to the literatures,[12,13] ESR signal having g-values of 2.043—2.002 with the sulfide catalysts could be attributed to the $\dot{S}_n$ radicals involving S_3^- anion radicals and/or the more long chain sulfur radical species stabilized on the sulfide surfaces. Recently, Yanagida et al.[9] have found the ESR signal having g-value of 2.011 with ZnS sols after UV irradiation at 77 K, attributing it to a hole center localized on the lattice S^{2-} sulfur ions, i.e., sulfur radicals mentioned above.

5. Effect of the Addition of Sulfur upon the Photocatalyzed Isomerization. ESR measurements suggest that the photo-formed $\dot{S}_n$ type radicals play a significant role in the photocatalyzed isomerization of 2-butene. So, the photocatalyzed isomerization of 2-butene has been investigated with the CdS catalyst involving 5 wt% of sulfur. The results in Fig. 7 show that the photocatalyzed isomerization of *cis*-2-butene toward *trans*-2-butene is enhanced with sulfur-modified CdS catalysts which had been pretreated in vacuum at higher temperature than 373 K after mixing sulfur. Since sulfur has higher vapor pressure than 1 Pa at the pretreatment temperatures, a part of the sulfur vapor (S_8) appears to deposite on strong adsorption sites of the catalyst surface. Thus, the enhancement of the photoisomerization by the addition of sulfur seems to be caused by the sulfur clusters such as S_8 deposited on the catalyst surface.

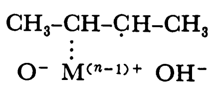
Discussion

From the photocatalyzed isomerization reactions of 2-butene over the various metal oxides[3-5] and Ti-Si binary metal oxide catalysts,[6] the following features were drawn: in the case of *cis-trans* isomerization of 2-butene, the photo-formed O^- hole centers play a significant role in the photocatalyzed isomerization to weaken the C=C double bond via the formation of the radical intermediate species



$$\underset{\vdots \atop O^-}{CH_3\text{-}CH}\text{-}\dot{C}H\text{-}CH_3 \qquad [I];$$

while in the case of the double bond shift isomerization, a concerted action of the photo-formed O^- hole center and the photo-formed $M^{(n-1)+}$ electron-trapped center as well as the surface hydroxyl groups plays a significant role in the isomerization to cause the double bond shift via the formation of the intermediate species[4]



$$CH_3\text{-}\underset{\vdots \atop O^-\ M^{(n-1)+}}{CH}\text{-}\underset{\atop OH^-}{\dot{C}H}\text{-}CH_3 \qquad [II].$$

Therefore, the *cis-trans* isomerization over the oxides is enhanced and the double bond shift isomerization decreases drastically, when the electron-trapping centers are existent in the catalyst. In other words, the photo-formed electron-hole pair states closely associate with the photo-induced double bond shift isomerization, while only the positive hole center, remained after capturing the photo-formed electron on the electron-trapping sites or agents added, participates in the photo-induced *cis-trans* isomerization of 2-butene.[6]

The facts that the intensity of ESR signal attributed to $\dot{S}_n$ type radicals increases with UV irradiation and that the photocatalytic isomerization of 2-butene is enhanced under UV irradiation suggest that the $\dot{S}_n$ type radicals play a significant role on the photocatalytic *cis-trans* isomerization over the sulfide catalysts. This suggestion is supported by the proposition by Yanagida et al.[9] that $\dot{S}_n$ radicals originated from surface defects like interstitial sulfur act as active sites for the photocatalyzed *cis-trans* isomerization. The $\dot{S}_n$ type radical species produced by the trapping of photo-formed holes by the lattice S^{2-} ions and/or sulfur clusters appear to participate in the *cis-trans* photoisomerization of 2-butene, in the manner similar to that of the O^- hole center with the oxide catalysts.[3-5] The photocatalyzed *cis-trans* isomerization of 2-butene over the sulfide catalysts seems to proceed as a result of opening of the C=C double bond of 2-butene via the interaction of the double bond with the photo-formed $\dot{S}_n$ type radicals, i.e., the same kind of intermediate species as [I] for the oxide catalysts.

The $\dot{S}_n$ type radicals exist inherently in the sulfide catalysts as seen in Figs. 5 and 6, as well as the case that the ESR signal ascribed to the trapped hole with ZnS (Nakarai) was observed before irradiation and increased on irradiation.[9] The *cis-trans* isomerization rate in the dark conditions over the various types of sulfide catalysts at 273 K strongly depends upon the concentration of the $\dot{S}_n$ type radicals. The increase of the ESR signal intensity for the $\dot{S}_n$ type radicals under UV irradiation results in the enhancement of the *cis-trans* isomerization. These results imply that the *cis-trans* isomerization of 2-butene in the dark conditions over the sulfide catalysts proceeds with the same mechanism as that of the photocatalyzed isomerization mentioned above. That is, the interaction of the C=C double bond of 2-butene with the $\dot{S}_n$ type radicals existing inherently in the catalysts after evacuated at the pretreatment temperatures results in the weakening of the double bond.

The photocatalyzed isomerization of 2-butene over the sulfides is inhibited with the addition of oxygen or NO molecules, as well as the case of the inhibition by oxygen on the photocatalytic *cis-trans* isomerization of olefins over sulfides in the liquid-solid system.[8,9] De Mayo et al.[8] have proposed that the inhibition by oxygen of the photocatalytic *cis-trans* isomerization of substituted styrenes over CdS in dichloromethane solution is due to the reaction of O_2^- with the cation intermediate of the styrenes. Yanagida et al.[9] have reported that the suppression of the photocatalytic isomerization of *cis*-2-octene over ZnS in aerated solution is due to the preferential capture of active sites by O_2 or O_2^- and due to the lasting degradation of active sites via photooxidation of ZnS to $ZnSO_4$.[14] On the other hand, the inhibition by added oxygen or NO molecules on the photocatalytic isomerization of 2-butene over the metal oxide catalysts such as ZnO[4] and TiO_2[5] in the gas-solid system was attributed to the reaction of the photo-formed active sites (O^- hole center) with O_2 or NO molecules to produce the anion radicals of $O_3^-(O^- + O_2 \rightarrow O_3^-)$ or NO_2^{2-} $(O^- + e^- + NO \rightarrow NO_2^{2-})$. The inhibition of the photocatalytic isomerization by O_2 or NO in the present system appears to be caused to scavenging of the $\dot{S}_n$ type radicals by these molecules, since the ESR signal intensity for the $\dot{S}_n$ radicals decreases with the addition of O_2 or NO.

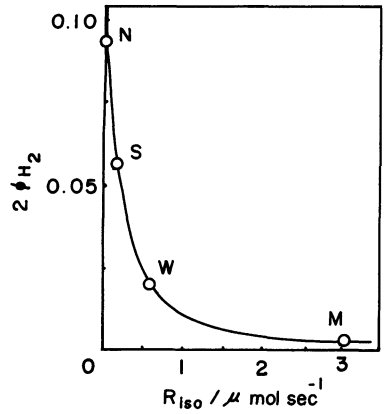


Fig. 8. Comparison of the twice of the quantum yield of H_2 evoluted from methanol-water solution ($2\phi_{H_2}$) with the initial rate of the photocatalyzed isomerization of *cis*-2-butene (R_{iso}) over commercial ZnS powders. N, S, W, and M mean the ZnS specimens obtained from Nakarai, Shimakyu, Wako, and Mitsuwa Chemicals Cos., respectively.

However, the addition of O_2 or NO molecules onto the sulfide catalysts led to partial inhibition of the photocatalytic isomerization, which is in contrast with the results obtained with the oxide catalysts. On the ESR measurements in the presence of O_2 or NO, no any appearance of new signals could be observed with the sulfide catalysts even after UV irradiation at 77 K, although the ESR signal for O_3^- or NO_2^{2-} species produced by the reaction of the O^- hole center with O_2 or NO was observed with the oxide catalysts.[4,5] These results suggest that the photo-formed hole center with the sulfides might be more stabilized on and/or near the surfaces of the sulfides than with the oxides. Therefore, the hole center on the sulfides might be less degradable than that on the oxides.

As shown in Table 1, the sulfide catalysts exhibit quite different photocatalytic activity for the *cis-trans* isomerization from each other. In connection with this problem, the photocatalytic activity of the sulfides for the photoisomerization reaction of *cis*-2-butene toward *trans*-2-butene has been compared with that for the H_2 evolution from the methanol-H_2O solution system made by Yanagida et al.[1] Figure 8 shows the relationship between the photocatalytic activities for the isomerization of *cis*-2-butene toward *trans*-2-butene and for the H_2 evolution reactions. The result clearly indicates that the catalyst having high activity for the isomerization exhibits low activity for the H_2 evolution reaction, though it would be difficult to discuss the reverse relation quantitatively, since the reaction systems are different from each other. It is well-known that the H_2 evolution results from the redox reaction, where photo-formed electron and hole participate in the reaction. Therefore, the result shown in Fig. 8 suggests that only the photo-formed hole closely associates with the *cis–trans* isomerization of 2-butene. In connection with such relationship, it should be also mentioned that the selectivity of the photocatalyzed isomerization toward 1-butene, where both photo-formed electron and hole participate in the reaction, reduces with increasing of the rate of the *cis–trans* isomerization with ZnS catalyst (Table 1), except for ZnS (Wako).

As described previously,[5] on the UV irradiation of TiO_2 or ZnO catalyst in the presence of 2-butene and water, the photohydrogenation (formation of n-C_4H_{10}) and photohydrogenolysis (formation of C_2H_6) products were observed together with the photoisomerization products (*cis*- or *trans*-2-butene and 1-butene), where the yields of the latter products decrease with increasing the amount of adsorbed water. In this case, it was characterized in the previous works[4–6,11] that the photo-formed electron and hole and/or photo-formed electron-hole pair states participate in the formations of C_2H_6 and 1-butene. On the UV irradiation of CdS or ZnS catalyst in the presence of *cis*-2-butene and water, however, no any hydrogenated products could be detected. This is the one of the most different features of the sulfide catalysts as compared with the oxides. As discussed above, this feature might be attributed to the facts that with the sulfides the concentration of the photo-formed electron-hole pair states is considerably suppressed by efficient trapping of photo-formed electron and/or hole with their trapping centers existing in the catalyst and that the reactivity of $\dot{S}_n$ type radicals is quite different from that of O^- hole center on the oxides.

On the photocatalytic activities of the metal sulfides for the isomerizations of 2-butene, it has been in general found that the *cis–trans* isomerization is very fast, but the double bond shift isomerization is much slow, in comparison with those of the metal oxide catalysts. The photo-formed radical species, $\dot{S}_n$ type radicals, play a significant role in the photoisomerization over the sulfides. The results suggest that this radical species have a quite long lifetime and are used repeatedly for the reaction. From these results together with the facts that the addition of O_2 or NO molecules leads to the inhibition of the photocatalyzed isomerization, but not to the complete inhibition, and $\dot{S}_n$ type radicals can be present stably in the catalyst even at around 573 K, it could be imagined that the photo-formed $\dot{S}_n$ type radical species as active sites for the *cis-trans* isomerization are present in the sulfur clusters on the surfaces and/or in the interstitial sites.

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