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Hydrogenation of Ethylene on a MoS_2 Catalyst

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The evacuated MoS_2 surface has two kinds of active sites with different degrees of coordinative unsaturation named B-sites and C-sites. The hydrogenation of ethylene, the exchange between D_2 and C_2H_4 and the H_2–D_2 equilibration proceed on the CH_2 and CH-sites, however, the BH-sites promotes the hydrogen exchange between C_2H_4 and C_2D_4. The hydrogen addition on the CH_2-sites should maintain the hydrogen molecular identity, but facile reverse process of the ethyl intermediate on the CH_2-sites lowers the conservation of the hydrogen molecularity in the ethane compared with the other olefins. By treating with H_2S, the C-sites on the surface are diminished, but the specific sites remained in the layer of the MoS_2 promote the H_2–D_2 equilibration.

It is known that molybdenum sulfide is an effective component of industrial catalysts for coal hydrogenation and the hydrodesulfurization reactions. In our series of works (*1–4*), it was confirmed that sites having different degrees of the coordinative unsaturation exhibit different catalytic abilities as proposed by Siegel (*5*). A typical example was found in the partial hydrogenation of acetylene and/or of the dienes over sulfided nickel catalyst, where the selective partial hydrogenation was strictly controlled by the reversible change of the degrees of coordinative unsaturation of nickel.

In a previous paper (*4*), it was demonstrated that the evacuated MoS_2 surface has two kinds of active sites, one is effective for the hydrogenation reaction and the other is only effective for the isomerization and/or the hydrogen mixing between olefins in the presence of hydrogen.

In order to make clear this feature of the MoS_2 catalyst, the hydrogenation of ethylene, the hydrogen mixing between C_2H_4 and C_2D_4 as well as between D_2 and C_2H_4, and the H_2–D_2 equilibration reaction have been attempted in this paper.

EXPERIMENTAL METHODS

The apparatus used in this experiment was a closed circulating system with a total volume of about 300 ml. A commercial MoS_2 power from Kanto Chemicals Co. was purified as follows; the MoS_2 powder was boiled in HCl solution for several hours, and was filtered off and washed with distilled water, after that, the powder was again boiled in NaOH solution (20%) for several hours, and was filtered off, washed with distilled water as well as with hot water, and dried in air. The impurities in this purified MoS_2 analyzed by atomic absorption, were (%): Fe, 0.02; Mg, 0.0015; Ca, 0.0077; Na, 0.012; Mn, 0.0003; Cr $<$ 0.0001; K $<$ 0.1. The structure of this MoS_2 powder was a typical 2H (hexagonal) layer structure as determined by X-ray diffraction. By evacuating the MoS_2 at

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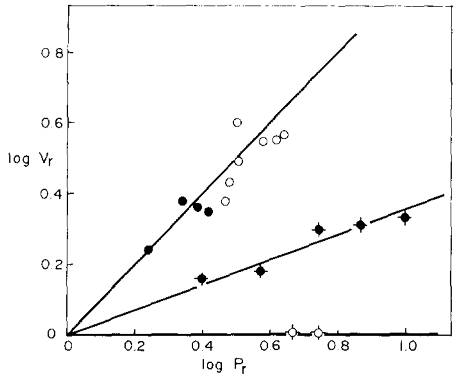


FIG. 1. Pressure dependences of the hydrogenation rate. P_r is the factor of the pressure change and V_r is the factor of the velocity change at the corresponding P_r. Dependence on hydrogen: (○—) 0°C; (●—) 60°C; dependence on ethylene: (ϕ- -) 0°C; (♦- -) 60°C.

about 450°C for several hours, the MoS_2 becomes active for the hydrogenation of ethylene, the hydrogen exchange between C_2H_4 and C_2D_4 as well as between D_2 and C_2H_4, and the H_2–D_2 equilibration. The surface area of the evacuated MoS_2 catalyst was 15 m²/g by the BET method with nitrogen adsorbent. Auger electron spectroscopic analysis of the evacuated MoS_2 gave no peaks other than Mo, S, C, and O, indicating no appreciable accumulation of the impurity metal on the surface by the activation procedure.

The analysis of ethylene and ethane were carried out in an on-line gas chromatograph using a silica gel column for the separation. H_2, HD, and D_2 was separated by freezing the hydrocarbons at liquid nitrogen temperature, and was subjected to the mass spectrometric analysis. The frozen hydrocarbons were vaporized, and the deuteroethylene in it was analyzed with a mass spectrometer with an ionization potential of 12.5 eV, at which no ionization of ethane occurs. The analysis of the deuteroethane was carried out by using a gas-chro mass spectrometer with an ionization voltage of 70 eV. The distributions of deuterium in the ethane were calculated by taking into account the isotope effect for fragmentation (*6*).

Perdeuteroethylene used in this experiment was prepared by deuteration of C_2D_2 on a Pt/asbestos catalyst, and was purified through a gas chromatographic separation, of which isotopic composition was C_2D_4, 94.2% and C_2D_3H, 5.8%. Ordinary ethylene was purified by freezing at liquid nitrogen temperature followed by vaporizing at dry ice–methanol temperature. H_2 gas was purified by diffusion through a silver–palladium thimble, and D_2 from a commercial cylinder was passed through a liquid nitrogen trap before use.

RESULTS

1. Evacuated MoS_2 Catalyst

The pressure dependence of the reaction rate was determined by raising the hydrogen pressure or the ethylene pressure abruptly during the course of the hydrogenation. As shown in Fig. 1, it is first order in hydrogen pressure at either 0 or 60°C, however, the order in ethylene pressure depended on the temperatures, zero order at 0°C and 0.36 order at 60°C. V_r in Fig. 1 is the ratio of the reaction rate after raising the pressure to that before the pressure was changed, and P_r is the ratio of the pressures after and before changing. Recognizing the different pressure dependencies of ethylene at 0 and 60°C, the deuteration of ethylene was carried out at both temperatures, and no appreciable differences were found in the deuterium distributions at 0 and 60°C, as shown in Table 1. The deuterium distributions in ethane, in ethylene, and in hydrogen are shown in Fig. 2. As shown in Fig. 2a, the deuterium distribution in ethane is obviously not in accord with the random distribution indicated by the broken lines, and the main species are d_2- and d_1-ethanes.

On the other hand, the random distribution is established in ethylene as shown in Fig. 2b, which is in accord with the ex-

TABLE 1

Deuterium Distributions in the Deuteration of Ethylene at 0 and 60°C on the MoS_2 Catalyst (1.0 g)[a]

Conversion (%)	Hydrogen			Ethylene					Ethane						
	H_2	HD	D_2	d_0	d_1	d_2	d_3	d_4	d_0	d_1	d_2	d_3	d_4	d_5	d_6
1.[b]															
1.9	0	6.4	93.6	92.8	6.6	0.6	0	0	6.0	39.6	52.0	2.4	—	—	—
	(0.1)	(6.2)	(93.7)	(93.4)	(6.4)	(0.2)	—	—	(17.6)	(35.4)	(29.8)	(13.3)	(3.4)	(0.5)	—
6.9	0.8	10.8	88.4	84.0	14.6	1.5	0	0	4.5	36.2	52.4	6.9	—	—	—
	(0.4)	(11.6)	(87.9)	(83.4)	(15.4)	(1.1)	—	—	(15.2)	(33.7)	(30.1)	(15.2)	(4.2)	(0.6)	—
2.[c]															
4.1	1.5	11.9	86.5	82.6	15.4	2.0	—	—	4.4	38.1	50.9	4.3	1.4	0.5	0.4
	(0.6)	(13.9)	(85.5)	(82.0)	(16.7)	(1.3)	—	—	(14.9)	(33.3)	(31.2)	(15.5)	(4.4)	(0.7)	(0)
12.6	3.6	24.2	72.4	64.6	29.5	5.9	—	—	5.6	33.4	50.4	7.3	2.2	0.6	0.6
	(2.4)	(26.2)	(71.4)	(64.7)	(29.8)	(5.1)	(0.4)	—	(13.3)	(31.8)	(31.9)	(17.0)	(5.1)	(0.9)	(0.1)

[a] The values in parentheses are random distributions.

[b] 0°C; C_2H_4 = 21.4 mm Hg, D_2 = 16.7 mm Hg.

[c] 60°C; C_2H_4 = 27.0 mm Hg, D_2 = 45.0 mm Hg.

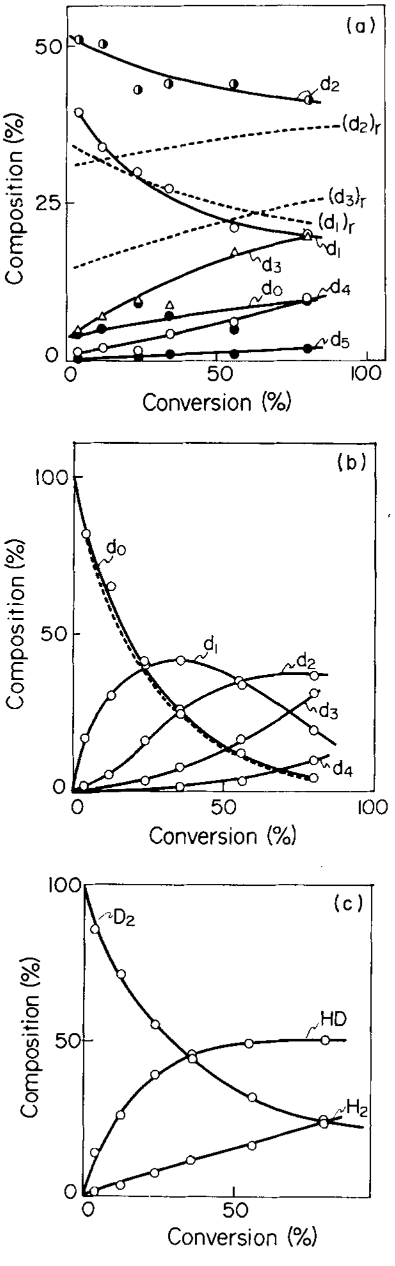


FIG. 2. The deuterium distributions in ethane (a), in ethylene (b), and in hydrogen (c) observed in the reaction of C_2H_4 and D_2 at 0°C on 1.0 g MoS_2. ((····) The calculated random distribution.

tremely rapid hydrogen exchange between C_2H_4 and C_2D_4 in the presence of hydrogen (*4*).

The H_2–D_2 equilibration during the hydrogenation of ethylene is much slower than the hydrogen exchange between C_2H_4 and C_2D_4, but is much faster than the exchange reaction between D_2 and C_2H_4, as a result, the deuterium distribution in hydrogen gives nearly equilibrated distribution as shown in Fig. 2c. More clear results revealing the rapid hydrogen mixing of ethylene as well as the rather rapid H_2–D_2 equilibration were shown in the reaction of a mixture of C_2H_4 and C_2D_4 with a mixture of H_2 and D_2 at 0°C, in which the hydrogen exchange of ethylene arrived at equilibrium within 2% conversion of hydrogenation (*3*).

The isotopic exchange between D_2 and C_2H_4 occurs several times faster than the hydrogenation reaction as is known from 7.2% of the deuteroethylene in 1.9% of the hydrogenation at 0°C. Accordingly, the relative catalytic activities of the evacuated MoS_2 for these reactions are described as; C_2H_4–C_2D_4 exchange $\gg$ H_2–D_2 exchange $>$ D_2–C_2H_4 exchange $>$ hydrogenation at 0°C. It should be emphasized that the hydrogen exchange reaction between C_2H_4 and C_2D_4 is markedly enhanced by addition of hydrogen as shown in Fig. 3, but the isotopic mixing between hydrogen and ethylene does not occur appreciably during the isotopic mixing of ethylene. These

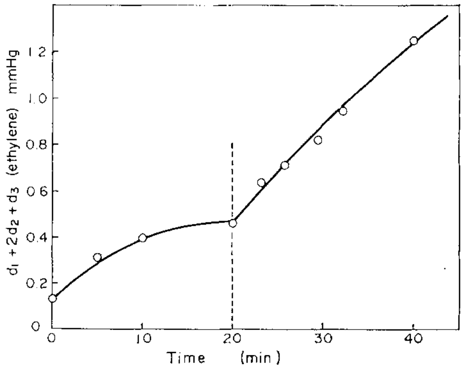


FIG. 3. Hydrogen promoting effect on the C_2H_4–C_2D_4 exchange reaction at room temperature. 3 mm Hg of a mixture of C_2H_4 and C_2D_4 was admitted to 0.2 g of MoS_2 at time 0, and 6 mm Hg of H_2 was added at 20 min.

findings reveal that the hydrogen mixing of ethylene may proceed through the associative mechanism, and the hydrogen bonded to the active sites is scarcely replaced with ambient hydrogen.

2. H_2S Treated MoS_2 Catalyst

In a previous paper (*4*), it has been confirmed that the evacuated MoS_2 catalyst has two kinds of active sites showing different catalytic abilities, one is active for the hydrogenation and the other is only effective for the isomerization reaction. If these different catalytic abilities are related to the different degrees of coordinative unsaturation of the active sites as has been proposed (*2, 3, 5*), the sites having the higher degrees of coordinative unsaturation, the active sites for the hydrogenation, might be diminished preferentially by the H_2S treatment. Unless otherwise stated, the MoS_2 evacuated at 450°C for several hours was treated with 0.25 to 0.5 mm Hg of H_2S for 1 to 2 min at 300°C, and was followed by evacuation at the same temperature for 15 to 20 min. By treating with H_2S, the catalytic activities of the MoS_2 decreased significantly for all the reactions, and the hydrogenation of ethylene as well as the D_2–C_2H_4 exchange reaction were so slow as to be negligible at room temperature, 0.66% of the hydrogenation in 51 hr.

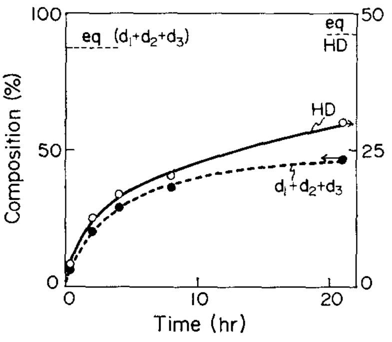


FIG. 4. The H_2–D_2 equilibration and the hydrogen exchange between C_2H_4 and C_2D_4 observed on the H_2S-treated MoS_2 (0.5 g) at room temperature. A mixture was composed of 42 mm Hg of H_2 and D_2 and 16 mm Hg of C_2H_4 and C_2D_4. The catalyst was treated by 1 mm Hg of H_2S at room temperature for 1 min and followed to 10 min evacuation.

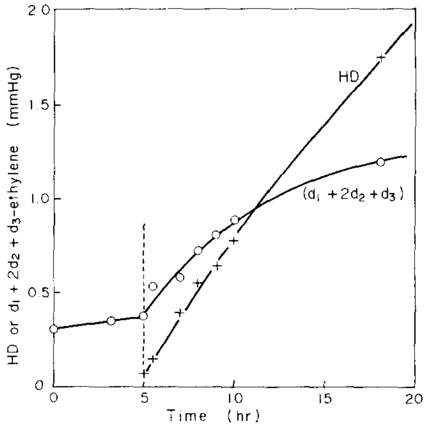


FIG. 5. The hydrogen promoting effect on the hydrogen exchange between C_2H_4 and C_2D_4 at room temperature on the H_2S-treated MoS_2 (0.5 g). 12.5 mm Hg of a mixture of C_2H_4 and C_2D_4 was admitted at time 0, and 20.5 mm Hg of a mixture of H_2 and D_2 was added at 5 hr.

A typical result when a mixture of C_2H_4, C_2D_4, H_2, and D_2 was admitted to the H_2S-treated MoS_2 catalyst is shown in Fig. 4, where only the C_2H_4–C_2D_4 exchange and the H_2–D_2 equilibration are observed. This result indicates that the activity sequence of the H_2S-treated MoS_2 differs from that of the evacuated MoS_2; H_2–D_2 equilibration > C_2D_4–C_2H_4 exchange ≫ hydrogenation, D_2–C_2H_4 exchange. It is interesting that the C_2H_4–C_2D_4 exchange reaction on the H_2S-treated MoS_2 also requires hydrogen as is confirmed in Fig. 5 by a remarkable hydrogen promoting effect. In Fig. 5, it is clear that the addition of a mixture of H_2 and D_2 brings about the HD formation by the equilibration in spite of the negligible D_2–C_2H_4 exchange, that is, the C_2H_4–C_2D_4 exchange reaction and the H_2–D_2 equilibration proceed independently with little mutual isotopic mixing, between hydrogen and ethylene.

Such unusual properties of the H_2S-treated MoS_2 is perceived in Fig. 6, in which ethylene has a very weak retardation

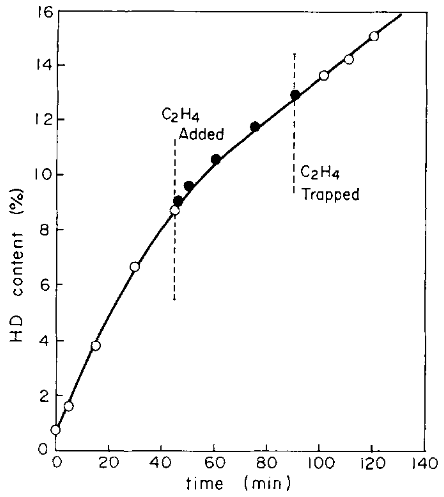


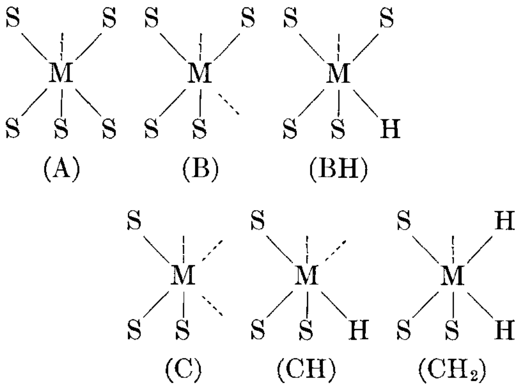
FIG. 6. Less retardation effect of ethylene on the H_2–D_2 equilibration taking place on the H_2S-treated MoS_2 at 90°C.

effect on the H_2–D_2 equilibration; this finding is in contrast with the striking retardation on the evacuated MoS_2, on which the contribution of the H_2–D_2 equilibration being similar to the H_2S-treated surface is very little.

DISCUSSION

It is well known that the deuteration of ethylene on the metal catalysts accompanies the hydrogen exchange between D_2 and ethylene, and so far, the deuteroethylene formation has been explained by the reverse process from the ethyl intermediate, that is, both the deuteroethylene formation and the hydrogenation of ethylene occur through the same reaction route provided by the associative mechanism.

In contrast with this, it was found on the sulfided nickel catalyst that the hydrogen mixing of olefins and/or the isomerization reaction of olefins, being promoted by hydrogen, takes place on the active sites on which no hydrogenation of olefins can take place (*2*, *3*). If this surface is contacted with acetylene, however, the active sites for the hydrogenation of acetylene as well as of olefins arise. These interesting phenomena have been well explained by the different coordinative unsaturation of the active sites such as proposed by Siegel (*5*). The sites on the sulfides or on the oxides can be described according to the degrees of coordinative unsaturation as follows:



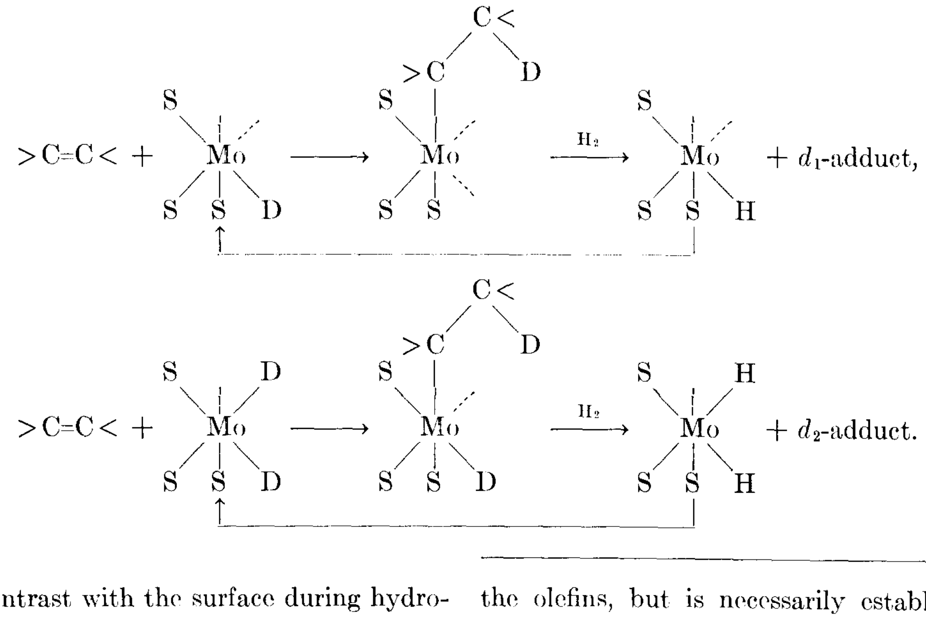
The MoS_2 used in the experiments has hexagonal structure characterized by sandwich-like layer form. If the stoichiometric crystallite is cleaved along the *c*-axis, various molybdenum ions are exposed on the newly formed surfaces, among which 4-coordinated molybdenum ions, the B-sites, are one of the most feasible sites. Furthermore, the B-site at the crystallite corner has a sulfur atom being singly bonded to molybdenum ion, which may be easily removed by high temperature evacuation and changes to the C-site.

In fact, there are two kinds of active sites on the evacuated MoS_2 surface, which may correspond to the B- and the C-sites (*4*). In contrast with the sulfided nickel, the sulfur atoms in the MoS_2 are not so mobile that the C-sites as well as the B-sites formed by evacuation remain on the surface, and the population of these sites on the MoS_2 might be the B-sites $\gg$ the C-sites, for the C-sites are preferential at the crystallite corners.

In our separate experiment, it was confirmed that the hydrogen exchange reaction of propene on the MoS_2 catalyst proceeds predominantly by the associative mechanism (*7*).

If the hydrogenation of ethylene and the hydrogen exchange of ethylene would proceed through the common ethyl intermediate, the extremely rapid hydrogen mixing of ethylene (*4*) arriving at the equilibration within 2% hydrogenation conversion should make lower the deuterium content on the surface during the reaction of ethylene with D_2, and should give d_0-ethane predominantly. That was not the case, but the main species were d_2-ethane and d_1-ethane as shown in Fig. 2a. Since Burwell (*9*) reported the selective d_2-adducts formation on the Cr_2O_3, the conservation of the hydrogen molecular identity in the hydrogenation reaction have been reported on the various oxides such as ZnO (*10*). TiO_2 (*11*), and Co_3O_4 (*12*).

Recently, it was found that the evacuated MoS_2 catalyst also has a similar property as the oxide catalysts (*13*), that is, the hydrogen molecularity is maintained nearly 100% in the hydrogenation of butadiene and 85% in the hydrogenation of the olefins except the especially poor conservation of ethylene as is known from Table 1 and Fig. 2a. On these interesting catalysts, the hydrogenation with a mixture of H_2 and D_2 was attempted, and the selective formation of the d_0- and the d_2-adducts was confirmed (*12, 13*). These results suggest that the hydrogenation of olefins occurs exclusively on the CH_2-sites and the hydrogen scrambling of ethylene proceeds on the BH-sites, that is, if the hydrogenation proceeds on the CH-sites the d_1-adduct should appear about twice of the d_0- and the d_2-adducts according to the following scheme:



In contrast with the surface during hydrogenation of olefins, CH-sites may be formed during the H_2–D_2 equilibration reaction, because C- and CH_2-sites are inactive for the equilibration (*5*). These facts may suggest that the apparent conservation of the hydrogen molecularity in the hydrogenation of olefins does not mean merely the irreversible hydrogen atom addition to the olefins, but is necessarily established by the structure of the CH_2-sites being isolated from each other on the surface (*13*). And, the difference in the conservation of the hydrogen molecularity observed in the hydrogenation of butadiene, butene, propene, and ethylene on the evacuated MoS_2 (*13*) might represent the facility for the reversibility of the half-hydrogenated intermediates on the C-type sites. Therefore, the ratio of the deuterium atoms entering ethylene molecule to the ethane formed reveals the ease of the reverse process by reference to the forward reaction, and the results shown in Table 1 indicate several times ease of the reverse process compared with the forward reaction.

It is quite reasonable that the C-sites may be reduced to the B-sites and/or to the A-sites by treating with H_2S. In fact, the reactions promoted by the C-type sites such as the hydrogenation of ethylene and/or the hydrogen exchange between D_2 and C_2H_4 do not occur appreciably on the H_2S-treated MoS_2. However, the equilibration between H_2 and D_2 observed in Figs. 4 and 5 are curious results, because the H_2–D_2 equilibration is not inhibited strictly. The retardation effect of ethylene is also different, that is, the H_2–D_2 equilibration taking place on the evacuated MoS_2 is entirely inhibited by a small amount of ethylene, but that on the H_2S-treated MoS_2 takes little retardation effect of ethylene as shown in Fig. 6. This result suggests that the equilibration between H_2 and D_2 may take place on CH-sites to which ethylene can not adsorb.

In a previous paper (4), it was shown that the H_2–D_2 equilibration occurs independent from the hydrogen mixing between C_2H_4 and C_2D_4 on the H_2S-treated MoS_2, which agrees quite well with the small retardation effect of ethylene on the H_2–D_2 equilibration shown in Fig. 6. We may arrive at a conclusion that the C-sites on the surface may be diminished effectively by the H_2S treatment, but those in the layer of the MoS_2 will survive. The spacing between layers, 2.96 Å, seems to be sufficient for hydrogen molecule penetration but not for ethylene molecule, as a result, the H_2–D_2 equilibration proceeds on the interior CH-sites with little retardation of ethylene and the C_2H_4–C_2D_4 hydrogen mixing is catalyzed by the BH-sites on the surface.

By assuming the model of the active sites having different degrees of coordinative unsaturation, the complicated deuterium distributions as well as the peculiar catalytic properties of the MoS_2 are well understood.

REFERENCES

1. Tanaka, K., *J. Catal.* **37**, 558 (1975).
2. Takeuchi, A., Tanaka, K., and Miyahara, K., *Chem. Lett.* 171, 411 (1974).
3. Takeuchi, A., Toyoshima, I., Tanaka, K., and Miyahara, K., *J. Catal.* **40**, 94 (1975); Takeuchi, A., Tanaka, K., and Miyahara, K., *J. Catal.* **40**, 101 (1975).
4. Okuhara, T., Sato, S., Tanaka, K., and Miyahara, K., *J. Catal.* **43**, 360 (1976).
5. Siegel, S., *J. Catal.* **30**, 139 (1973).
6. Amenomiya, Y., *Canad. J. Chem.* **46**, 174 (1968).
7. Okuhara, T., Kondo, T., Tanaka, K., and Miyahara, K., *Shokubai* (*Catalyst*) **18**, 87 (1976).
8. Collman, J. P., *Accounts Chem. Res.* **1**, 136 (1968).
9. Burwell, R. L., *J. Amer. Chem. Soc.* **82**, 6272 (1960).
10. Kokes, R. J., *J. Amer. Chem. Soc.* **90**, 6859 (1968); *J. Phys. Chem.* **73**, 2436 (1969).
11. Lake, I. J. S., and Kemball, C., *Trans. Faraday Soc.* **63**, 2535 (1970).
12. Tanaka, K., Nihira, H., and Ozaki, A., *J. Phys. Chem.* **74**, 4510 (1970).
13. Okuhara, T., Tanaka, K., and Miyahara, K., *Chem. Commun.* 42 (1976).