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Olefin Metathesis Reaction on a MoS_2 Catalyst

Since Bank and Bailey's discovery of a new type of catalytic disproportionation reaction of olefins (*1*), a variety of mechanisms for the olefin metathesis reaction has been proposed from experimental and theoretical considerations (*2*). In this communication, the olefin metathesis reaction has been found to take place on a rather pure molybdenum sulfide evacuated at about 450°C for several hours. The valence state and the configuration of the active sites are indispensable to establish the reaction mechanism. Accordingly, the catalysis by well-defined materials should be interesting, but, to the best of our knowledge, pure MoS_2 has not been reported in the metathesis reaction, although poor activity was reported for MoS_2 supported on Al_2O_3 or SiO_2 (*3*). Molybdenum sulfide used in this experiment has 2H structure (hexagonal) by X-ray diffraction, and its surface area is 15 m^2/g by the BET method. Impurities analyzed by atomic absorption analysis were (in percentages): Fe, 0.02; Mg, 0.0015; Ca, 0.0077; Na, 0.012; Mn 0.0003; Cr, <0.0001; and K, <0.1.

In a previous cohydrogenation study of C_2H_4 and C_2D_4 on MoS_2, the metathesis reaction forming d_2-ethylene was smeared by the rapid hydrogen scrambling in ethylene (*4*). If a mixture of $^{12}C_2H_4$ and $^{13}C_2H_4$ was contacted with the MoS_2, however, an apparent metathesis reaction of ethylene was observed at room temperature, as shown in Fig. 1. In this experiment, the total pressure of ethylene was 2.5 mm Hg in a closed circulating system having volume of about 300 ml.

From systematic studies of the isotopic scrambling in ethylene, propylene, 1-butene, and 2-butene on MoS_2 by using microwave spectroscopy, it has been derived that the olefins having vinyl groups, such as 1-butene, propylene, and ethylene, exchange their vinyl hydrogens selectively and rapidly, but the hydrogen scrambling in 2-butene is extremely slow compared with that of the vinyl hydrogens (*5*). Therefore, by using a mixture of *cis*-2-butene-d_0 and *cis*-2-butene-d_8, the metathesis reaction of *cis*-2-butene was attempted. The result for a mixture of *cis*-C_4H_8 and *cis*-C_4D_8 (5 mm Hg) containing a mixture of 5 mm Hg of H_2 and D_2 ($H_2/D_2 = 1$) is shown in Fig. 2, where the reaction was carried out at room temperature over 0.1 g of the MoS_2 catalyst. Peculiarly high butene-d_4 is obtained in either *cis*-2-butene or *trans*-2-butene; however, 1-butene containing a vinyl group gives more extensive hydrogen scrambling than that in 2-butene. This characteristic deuterium distribution in butene isomers was also obtained in the absence of hydrogen. If we compare the values of d_4/d_1 or d_4/d_7 in *cis*-butene with that of *trans*-butene, more extensive isotopic mixing in *trans*-butene than in *cis*-butene may be

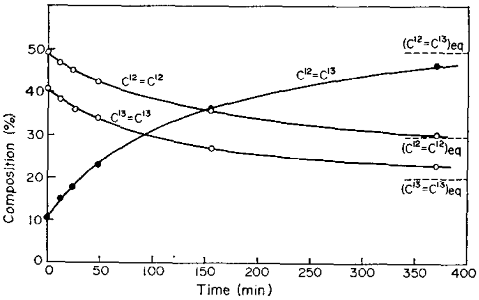

FIG. 1. Metathesis of ethylene on MoS_2 at room temperature.

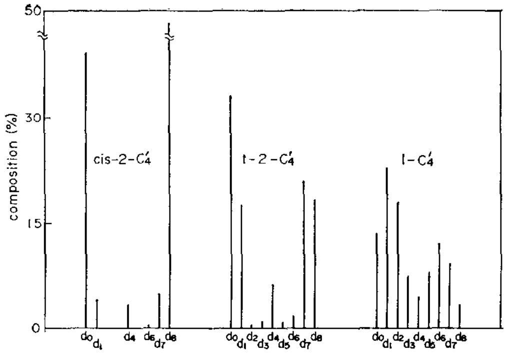

FIG. 2. Metathesis between *cis*-2-butene-d$_8$ and *cis*-2-butene-d$_0$ at room temperature. Compositions after analysis are: *cis*-2-butene, 59.0%; *trans*-2-butene, 37.3%; and 1-butene, 3.1%.

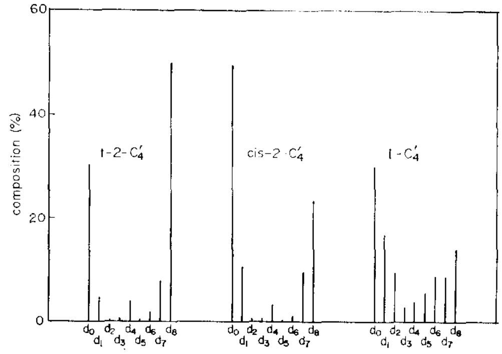

FIG. 3. Metathesis between *trans*-2-butene-d$_8$ and *trans*-2-butene-d$_0$ at room temperature. Compositions after analysis are: *trans*-2-butene, 74.4%; *cis*-2-butene, 24.0%; and 1-butene, 1.6%.

recognized, as shown in Fig. 2. On the contrary, in the reaction of *trans*-2-butene-d$_0$ and *trans*-2-butene-d$_8$ (Fig. 3), *cis*-butene exchanges more extensively than does *trans*-butene. These facts may indicate the existence of the direct conversion from *cis*-butene to *cis*-butene as well as from *trans*-butene to *trans*-butene by a metathesis reaction on the MoS$_2$ catalyst. WCl$_6$–C$_4$H$_9$Li (*6*) and MoCl$_2$(NO)$_2$(C$_5$H$_5$N)$_2$–C$_2$H$_5$AlCl$_2$ (*7*) have been known to exhibit stereoselective metathesis of 2-pentene; *cis*-2-pentene gives *cis*-2-butene selectively, while *trans*-2-pentene may give *trans*-2-butene, and the preferential reaction of *cis*-olefins results in stereoselective metathesis. The results on the MoS$_2$ catalyst perhaps indicate a similar type of stereoselective meththesis. The products of the metathesis reaction of propylene and of 1-butene carried out on 3 g of MoS$_2$ are summarized in Table 1. As the MoS$_2$ is active for the isomerization of the products, the stereoselectivity of the metathesis on the MoS$_2$ is smeared, but the values of *trans*-2-butene/*cis*-2-butene may suggest a *cis*-preferential reaction on MoS$_2$.

The MoS$_2$ catalyst evacuated at 450°C for several hours has two kinds of active sites, one is effective for the isomerization and the hydrogen isotopic mixing of olefins, and the other is active for the hydrogenation reaction (*8*), and these phenomena may be explainable by assuming different degrees of coordinative unsaturation of the active sites (*9*). The valence state and the coordinative unsaturation of the active sites for the metathesis reaction are an im-

TABLE 1

Disproportionation on MoS$_2$ (3 g) at room temperature

Reactant	Reaction time	Compositions (%)									*t*-C$_4'$/*c*-C$_4'$
		C$_2'$	C$_3$	C$_3'$	C$_4$	1-C$_4'$	*t*-C$_4'$	*c*-C$_4'$	*t*-C$_5'$	*c*-C$_5'$	
C$_3$H$_6$	17.5 hr	15.8	0.3	66.8	—	2.3	9.4	5.4	—	—	1.7
1-C$_4$H$_8$	3 min	0.2	—	0.5	—	81.8	12.2	5.3	—	—	2.3
	25 min	0.1	—	4.2	—	17.1	56.1	21.1	1.4	—	2.6
	120 min	0.2	—	11.9	—	2.8	55.5	21.3	5.6	2.5	2.6

portant problem (*10*), and, in conformity with the anisotropy of MoS_2 having the layered structure, studies on a single crystal would be desirable.

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TOSHIO OKUHARA
KEN-ICHI TANAKA

Research Institute for Catalysis
Hokkaido University
Sapporo, Japan

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