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LETTERS TO THE EDITORS

Comments on the Isomerization of Butenes on Co_3O_4 and Siegel's Model

Siegel's model (*1*) represents a correlation between the degree of coordinative unsaturation of active sites and their catalytic ability. This model has been established in a series of reactions catalyzed over sulfurated nickel (*2*). If this model is applied to the isomerization and the hydrogenation of butenes on Co_3O_4 reported by Fukushima and Ozaki (*3*), it may help to understand the deuterium distributions in butenes and in butane.

In a previous paper (*4*), it was demonstrated that the major part of preadsorbed hydrogen on Co_3O_4 does not take part in either the H_2–D_2 exchange reaction or in the ethylene hydrogenation. On the contrary, Fukushima and Ozaki (*3*) emphasized the participation of preadsorbed hydrogen in the isomerization of butenes in accordance with the differences of HD and d_1-butene formation on H_2-preadsorbed and D_2-preadsorbed Co_3O_4. However, if one takes into account the velocity of the H_2–D_2 equilibration reaction over Co_3O_4 arriving at equilibrium in less than a few minutes (*4*), the slow isotopic mixing between D_2 and preadsorbed hydrogen observed by Fukushima and Ozaki is probably responsible for the isotopic contamination of the hydrogen on the active sites by the inactive hydrogen preadsorbed on other than active sites. The perturbation by this contamination may be negligible in the rather rapid reactions as shown in Figs. 1 and 2. Figure 1 shows a correlation between HD formation and isomerization of 1-butene in the presence of D_2. No distinguishable differences in the HD formation are observed on H-surface and on D-surface. Figure 2 shows a relation between the amount of HD formed and that of 2-butene-d_1, the isomerized products, which undoubtedly indicates the formation of equal amounts of HD and 2-butene-d_1 during the isomerization reaction, however, 1-butene-d_1 has no such relation as shown in Fig. 2 with crosses. Figure 2 also reveals no detectable differences between the H_2 preadsorbed surface and the D_2 preadsorbed surface.

The low deuterium concentration in the isomerized products indicates the repeated use of active hydrogen and the slow isotopic contamination by the preadsorbed hydrogen or deuterium. As Fukishima and Ozaki pointed out, the isomerization is rather rapid, though the deuteration of butene gives more than 80% butane-d_2. These facts seem difficult to explain by the ordinary stepwise mechanism via a common intermediate on the same active sites as Fukushima and Ozaki said. They excluded the existence of the two kinds of active sites on Co_3O_4 in their paper, but their data prompt us to consider the two types of sites proposed by Siegel (*1*). Siegel's model has recently been established on sulfurated nickel catalyst (*2*) and also on MoS_2 catalyst (*5*).

A sulfurated nickel surface is only active for the isomerization of butenes or for the isotopic mixing of C_2H_4–C_2D_4, but is inac-

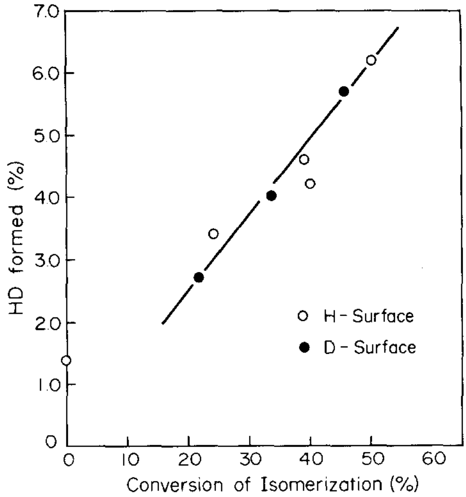

FIG. 1. HD formation and the isomerization of butene in the reaction of D_2 and butenes over the H_2 and D_2 preadsorbed surfaces.

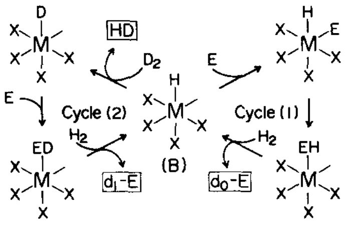

FIG. 3. Isomerization on BH sites.

tive for the hydrogenation of ethylene, butene and acetylene, and for the exchange reaction of D_2 with C_2H_4 or C_4H_8. However, by contacting the surface with acetylene, it becomes active with some induction time for the hydrogenation reactions as well as for the H_2–D_2 equilibration and the D_2–C_2H_4 or D_2–C_4H_8 exchange reactions. These features of the sulfurated nickel catalyst are well explained by the degree of coordinative unsaturation of active sites suggested by Siegel, that is, the active sites for the isomerization has two coordinative unsaturation (type BH), which are converted to three coordinative unsaturation sites (type CH), which are active for the hydrogenation, by displacing sulfur atoms with acetylene.

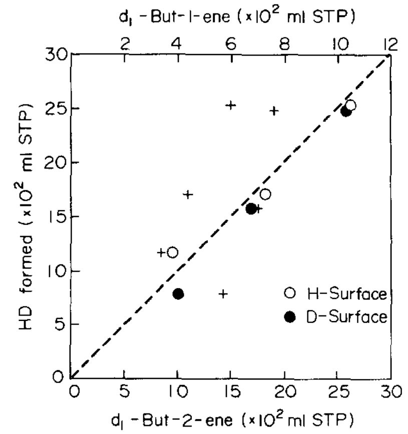

FIG. 2. The amount of HD formed and that of butenes-d_1. (○,●) 2-butenes-d_1; (+) 1-butene-d_1.

If the isomerization of butenes on Co_3O_4 mainly takes place over "type BH" sites, having little activity for hydrogenation, the relation is well understood. That is, the isomerization proceeds by catalytic cycle (1), and the equal amounts of HD and 2-butene-d_1 are produced by cycle (2) at times (Fig. 3). The hydrogenation of butene producing butane-d_2 proceeds on "type CH" sites, and the reverse process from butyl intermediate gives equal amount of butenes-d_1 and H atom on the CH sites, and H atom on the sites will come into butane-d_1 (EHD in Fig. 4). As the preadsorbed hydrogen on Co_3O_4 does not participate in the reactions, the following equation should be established in the reaction of D_2 and butene:

$$(\text{butenes-}d_1) + (\text{butane-}d_3) = (\text{HD}) + (\text{butane-}d_1),$$

where ( ) is the amount of the corresponding molecules. In the present case, (butane-d_3) is negligible and (HD) = (2-butenes-d_1) from Fig. 2, accordingly, (1-butene-d_1) should be equal to (butane-d_1).

Recalculation of Fukushima and Ozaki's data gives the following values (×10^2 ml STP).

Run	2	3	4	5	6	7
1-Butene-d_1	3.4	4.3	6.0	5.7	7.0	7.6
Butane-d_1	4.7	11.0	14.4	3.1	6.1	10.1

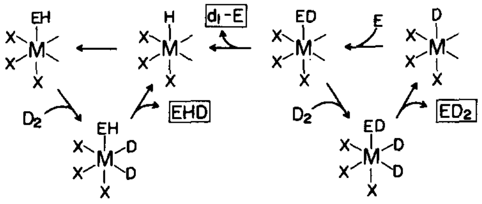

FIG. 4. Hydrogenation on CH sites.

If the hydrogenation takes place on type CH sites and the reverse process on these sites produces 1-butene-d_1, the equal amount of butane-d_1 and 1-butene-d_1 formation is quite reasonable. Fukushima and Ozaki regarded the deviation of the deuterium balance as "in coorperation of prechemisorbed hydrogen," however, the disagreement of the two values, 1-butene-d_1 and butane-d_1, may be due to insufficient accuracy of butane analysis by mass spectrometer.

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