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Reactivity of Preadsorbed Hydrogen on Co_3O_4

In a previous paper from our laboratory, it was reported that preadsorbed hydrogen H(a) on Co_3O_4 did not exchange with D_2 in a 60 min period at room temperature (*1*). After this report, Ono *et al.* (*2*) showed that the H(a) exchanged slowly with D_2 even at 0°C. Our later study disclosed that a part of H(a) is very active for the butene isomerization while it is rapidly displaced by butene, resulting in a drastic reduction of the isomerization activity. Thus we reexamined the previous result and found that even after the treatment with butene, the reaction of H(a) with D_2 gave a detectable amount of HD within 30 min at room temperature as reported (*3*). There was a disagreement with the previous result. However, what we emphasized in the recent paper was the role of active part of H(a), the incorporation of which is detectable only in the very beginning of the isomerization run.

The experiment data adopted by Tanaka in his letter are concerned with the surface which is freed from the active H(a) by treatment with butene. Even on such surface, the exchange of H(a) with D_2 takes place slowly, as mentioned above, in the absence of butene. In the presence of butene, however, the exchange seemed to be less extensive as shown by Tanaka in Fig. 1 of his letter, whereas there was an unignorable difference in the 1-butene-d_1 formations over the H- and D-surfaces, which is veiled in Fig. 2 of the letter and shown in Fig. 1 of this letter. It is clear that the formation of 1-butene-d_1 is also parallel to that of HD over the H-surface, while there is an additional amount of 1-butene-d_1 formed on the D-surface. This difference must be caused by the incorporation of preadsorbed D.

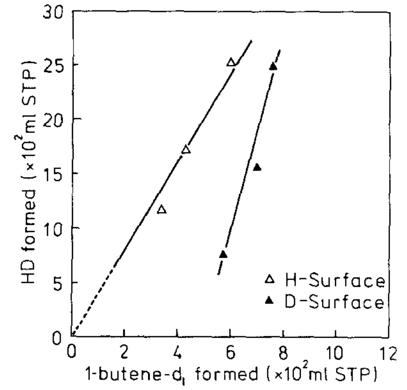

FIG. 1. The correlation between the amounts of HD and 1-butene-d_1 formed.

Tanaka claimed that the isomerization takes place over "type B" sites of Siegel's model (*4*) without accompanying hydrogenation. The isomerization scheme through cycle (1) and (2) is essentially the same as ours (*3*), whereas a disagreement is found in the scheme of butane-d_1 formation. We proposed that butane-d_1 is formed on the isomerization site by reaction with adjacent hydroxyl group, while Tanaka claimed that it can occur on the hydrogenation site which is characterized by butane-d_2 formation. However his scheme is evidently inconsistent with the well-established "paired addition" which was proved by the hydrogenation with H_2–D_2 mixture (*1*). The correlation among the amounts of deuterated species was already pointed out by us in the paper on the ground of our scheme. The result was approximately in agreement with this correlation (*3*).

The validity of Siegel's model has also been examined on the Co_3O_4 catalyst in terms of H_2–D_2 exchange and will be reported very soon.

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