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# Evidence for Two Kinds of Active Sites on a Molybdenum Sulfide

Molybdenum sulfide is an effective component of industrial catalysts for hydrodesulfurization and coal hydrogenation, and many practical studies have been made but few fundamental experiments have been done to make clear the characteristics of $MoS_2$ catalyst.

This brief paper gives evidence for two kinds of active sites on the $MoS_2$ having different catalytic abilities. The $MoS_2$ powder used in this experiment has hexagonal layer structure (2H) by X-ray diffraction, and its surface area is 15 $m^2/g$ by BET method with nitrogen adsorbent. Atomic absorption analysis showed the presence of the following impurities (%): Fe, 0.02; Mg, 0.0015; Ca, 0.0077; Na, 0.012; Mn, 0.0003; Cr, <0.0001; and K, <0.1. Evacuation at high temperature is an important procedure for activation of the $MoS_2$ catalyst, and evacuation at ca. 400°C for several hours enhanced the catalytic activities greatly for such reactions as the hydrogenation of olefins and of butadiene, the hydrogen isotopic exchange reactions of $H_2$–$D_2$, $D_2$–$C_2H_4$, and $C_2H_4$–$C_2D_4$, the isomerization of butenes, and the metathesis reaction of olefins at room temperature.

The catalytic activities of the evacuated $MoS_2$ for the hydrogen scrambling in olefins as well as for the isomerization are markedly increased by hydrogen addition; however, the isotopic exchange between $D_2$ and the olefins is rather slow. In this sense, the hydrogen promoting effects observed on $MoS_2$ is a kind of cocatalysis of hydrogen as has been observed on $Co_3O_4$ (*1*) and on sulfided nickel (*2*), and is evidence for a half-hydrogenated intermediate in hydrogen scrambling in olefins on the $MoS_2$.

As shown in Fig. 2, the hydrogen scrambling in ethylene over the $MoS_2$ is so rapid in the presence of hydrogen as to arrive at the random distribution within a hydrogenation conversion of 1%. The relative activities of the $MoS_2$ for the various reactions observed in a mixture of $C_2H_4$, $C_2D_4$, $H_2$, and $D_2$ gave a sequence of $C_2H_4$–$C_2D_4$ exchange $\gg$ $H_2$–$D_2$ exchange $>$ $D_2$–$C_2H_4$ exchange $\simeq$ hydrogenation at 0°C.

If both the hydrogenation of ethylene and its hydrogen scrambling reaction proceed on common active sites, $d_0$-ethane would be the main product in the reaction of $C_2H_4$ with $D_2$ (*3*), because the deuterium content in the adsorbed hydrogen is lowered greatly. The deuterium distribution in ethane for the reaction on the $MoS_2$ (30 mmHg of $C_2H_4$ and 47 mmHg of $D_2$) at 0°C, however, was 50.9% (50.4) of $d_2$-ethane, 38.1 (33.4) of $d_1$-ethane and 4.3 (7.3) of $d_3$-ethane at a conversion of 4.1%. The values in parentheses are the composition at a conversion of 12.6%.

The fact that the main species are $d_2$-ethane and $d_1$-ethane instead of $d_0$-ethane strongly suggests the existence of the two kinds of active sites having different catalytic abilities. Siegel (*4*) succeeded in explaining the same phenomena observed on the oxide catalysts such as $Cr_2O_3$ and $Co_3O_4$ by assuming different degree of coordinative unsaturation of the active sites. The authors (*2*) have reported experimental evidence for the reversible change of the degree of coordinative unsaturation of the active sites on the sulfided nickel catalyst, which controls the specific selectivity for the partial hydrogenation of acetylene and of poly-olefins. Taking these results into account, the hydrogen exchange reaction of ethylene is catalyzed by the sites having two degrees of coordinative unsaturation (B-site), while the catalytic hydrogenation of ethylene can take place on the sites having three degrees of coordinative unsaturation (C-site).

The rapid hydrogen scrambling of ethylene but the slow hydrogen exchange between $D_2$ and $C_2H_4$ on the $MoS_2$ indicates that the hydrogen atom on the B-site does not exchange as rapidly with gas phase hydrogen, so $d_0$-ethyl is the main species on the B-sites during reaction of $C_2H_4$ with $D_2$ as has been recognized on $Co_3O_4$ (*1*) and on the sulfided nickel (*2*). On the contrary, the half-hydrogenated intermediates on the C-sites contain a *d*-atom with rather high probability, which results in $d_2$-ethane and $d_1$-ethane formation. These differences in the intermediates on the two active sites are shown schematically in Fig. 1a.

Clearer evidence for the two different active sites on the $MoS_2$ has been obtained in the reaction of *n*-butene with $D_2$. The isomerization of butene was promoted remarkably by $D_2$ addition, but few deuterium atoms were contained in the isomerized products, that is, more than 90% of the isomerized products were $d_0$-butenes. In contrast with the isomerized products, simultaneously formed butane was composed of $d_2$-butane more than 80%. These results suggest that the intermediate in the hydrogenation on the C-sites is undoubtedly $d_1$-butyl, while the intermediate in the isomerization on the B-sites is $d_0$-butyl as shown in Fig. 1b.

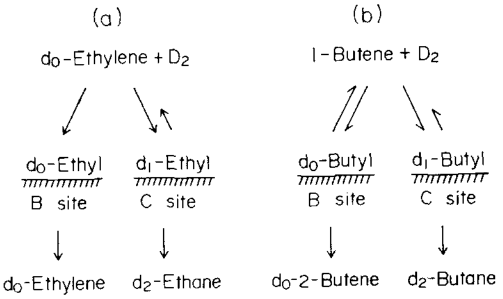

FIG. 1. The distinct half-hydrogenated intermediates on B-sites and on C-sites. (a) Ethylene and (b) 1-butene.

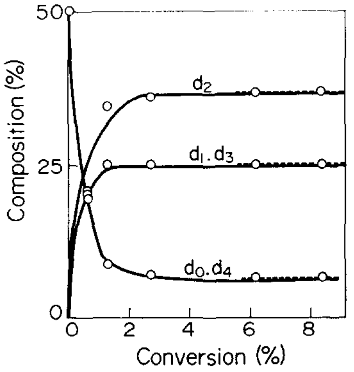

FIG. 2. Isotopic mixing between $C_2H_4$ and $C_2D_4$ in the presence of hydrogen at 0°C.

Furthermore, different hydrogen pressure dependence was observed on these two reactions, the hydrogenation and the isomerization taking place over different active sites as shown in Fig. 3. It was found that the hydrogenation rate is nearly first order in hydrogen pressure but isomerization is nearly zero order.

This experimental evidence confirms the existence of two kinds of active sites on the $MoS_2$, which may have different degree of coordinative unsaturation. In order to erase the C-sites, having a higher degree of coordinative unsaturation, the evacuated $MoS_2$ was treated with $H_2S$ of 0.25–0.5 mmHg for 1–2 min at 300°C.

The $H_2S$ treatment diminishes the catalytic activity of $MoS_2$ for both the hydrogenation and the hydrogen exchange reaction of ethylene. An interesting change has been observed on the activity sequence of the $MoS_2$ for a series of reactions: $C_2H_4$–$C_2D_4$ exchange $\gg$ $H_2$–$D_2$ exchange $>$ $D_2$–$C_2H_4$ exchange $\simeq$ hydrogenation on the evacuated $MoS_2$, and $H_2$–$D_2$ exchange $>$ $C_2H_4$–$C_2D_4$ exchange $\gg$ hydrogenation

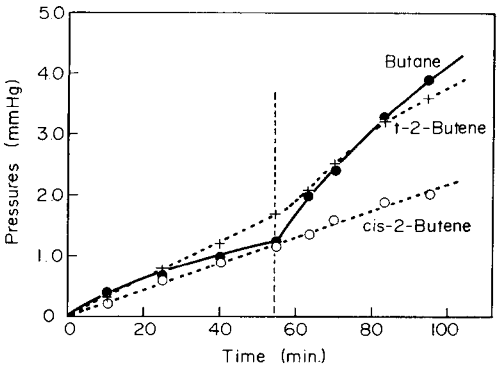

FIG. 3. Hydrogen pressure effects on the hydrogenation of 1-butene and on the isomerization of 1-butene at room temperature [(– – –) (vertical)] Hydrogen pressure was jumped from 9.26 to 77.3 mmHg.

on the $H_2S$-treated $MoS_2$. In the previous work, both the hydrogenation and the $H_2$–$D_2$ equilibration reaction were shown to take place on the C-sites (*1*, *2*, *4*). If this is true on the $MoS_2$ catalyst, the activity sequence of the $H_2S$-treated $MoS_2$, the $H_2$–$D_2$ exchange $\gg$ hydrogenation, is a strange result. In order to throw light on this strange phenomenon, a mixture of $H_2$, $D_2$, $C_2H_4$, and $C_2D_4$, adjusted to the different values of $D_2/(D_2 + H_2)$ and $C_2D_4/(C_2D_4 + C_2H_4)$, was admitted to the $H_2S$-treated $MoS_2$ at room temperature. The deuterium fractions in hydrogen and in ethylene, having been adjusted to the different equilibrium points, show no trend to approach each other even if both the hydrogen equilibration and the ethylene exchange reaction proceed as shown in Fig. 4.

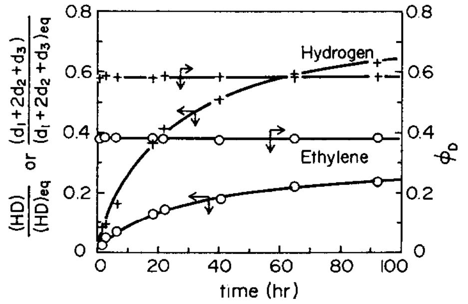

FIG. 4. The hydrogen isotopic mixing in a mixture of $H_2$, $D_2$, $C_2H_4$, and $C_2D_4$ at room temperature over a $H_2S$-treated $MoS_2$ catalyst.

It may be reasonable that $H_2S$ treatment of the evacuated $MoS_2$ diminished the C-sites on the surface effectively, but the C-sites within the layer of the $MoS_2$ have survived. The observed independent hydrogen mixing of the $H_2$–$D_2$ and the $C_2H_4$–$C_2D_4$, and the specific activity for the $H_2$–$D_2$ equilibration are well explained by the C-sites in the layer structure of the 2H–$MoS_2$, because its 2.96 Å spacing is sufficient for hydrogen penetration but not for the ethylene molecule. As a result, only the $H_2$–$D_2$ equilibration can proceed selectively on the C-sites in the layer structure, but neither the hydrogenation nor the exchange reaction of $D_2$–$C_2H_4$ can take place there. However, the isotopic hydrogen mixing in ethylene is catalyzed on the B-sites remaining on the $H_2S$-treated surface.

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