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Hydrogenation and Isomerization of Disodium Maleate in the Solid Phase over Fine Nickel Powder

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Synopsis. Disodium maleate was converted to a mixture of disodium maleate, fumarate, and succinate in the solid phase when particles of the starting material were kept in contact with fine nickel powder pretreated with hydrogen gas at 200 °C.

Solid surfaces have been noted as being possible sites for organic or inorganic reactions. Many gas- and liquid-phase reactions over solid surfaces have been intensively studied, especially regarding the research field of heterogeneous catalysis. Recently, some organic reactions in the solid phase have been reported.[1] In solid-phase reactions, solid reactants are mechanically mixed, and the reactions are carried out without the use of solvents. These reactions could be considered to be reactions between two solid surfaces. They have been shown to be unique, especially concerning areas of regio- and stereo-chemistry.

It is well known that transition metals, such as Pt, Pd, and Ni, dissociate hydrogen molecules into atomic or ionic hydrogens that react with neighboring substances in the gas or liquid phase. With respect to solid-phase reactions, in which the surfaces of transition metals take part, it is noteworthy that the dissociated hydrogens on a transition metal surface migrate to metal oxides that are used as either the supports or diluents of transition metal catalysts, and partially hydrogenate the oxides to bronzes.[2] Lamartine et al. reported on the solid-phase hydrogenation of organic compounds over the surfaces of transition metals; that is, the spillover hydrogens from Pt, Pd, Rh, Ru, and Ni were applied to the solid-phase hydrogenation of thymol to menthones(mixture of 2 isomers) and menthols (mixture of 4 isomers).[3] Dissociated hydrogens, which migrate through substrate particles from the catalysts, might react with solid substrates separate from the catalyst surface. For a better understanding of the reaction mechanism of solid-phase hydrogenation over transition metals, it is essential to employ a simple reaction giving one hydrogenation product as the standard reaction. In this work we attempted solid-phase hydrogenation of the C=C bond with a reaction producing only one hydrogenation product.

Results and Discussion

We chose the hydrogenation of disodium maleate in the solid phase over fine nickel powder as the standard reaction in this study. This choice was made based on the following facts:

1) The hydrogenation of an aqueous solution of disodium maleate over nickel catalysts gives disodium succinate as the only hydrogenation product.

2) As shown in Table 1, the melting points of disodium maleate, disodium succinate, and the mixture (1/1) of disodium maleate and succinate are very high.

Table 1. Melting Points of Disodium Maleate, Disodium Succinate, and Their Mixture (1/1)

Sodium salt	Melting point/°C
Maleate	>300 (Decomp)
Succinate[a]	>300 (Decomp)
Mixture(1/1)	>300 (Decomp)

a) Hexahydrate.

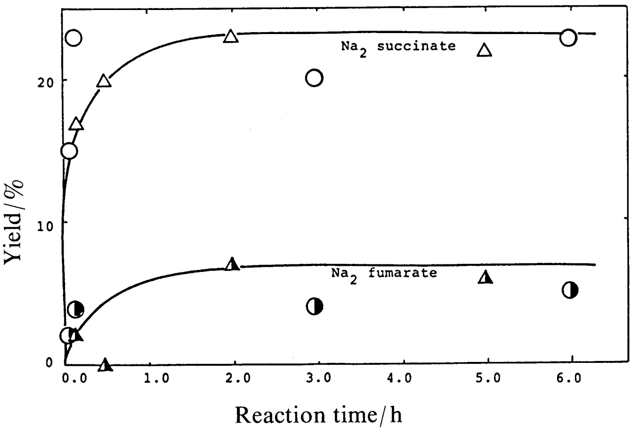

Fig. 1. Dependence of the hydrogenation and isomerization yields on the reaction time.
Catalyst: Ni pretreated with H_2, 200 mg.
○ ◑: under a H_2 atmosphere,
△ ▲: under an Ar atmosphere.

Fine nickel powder purchased commercially was treated with hydrogen gas at 200 °C before it was employed for the hydrogenation of sodium maleate. Most of nickel oxides on the surface were eliminated in this procedure. The H_2-treated nickel showed the ability to hydrogenate disodium maleate in the solid phase.

Figure 1 shows the relationship between the reaction time and the hydrogenation yield, when the reaction was carried out under either a hydrogen or argon atmosphere. Hydrogenation proceeded rapidly and the hydrogenation yield reached around 20% within 10 min, even under an argon atmosphere. This fact suggests that disodium maleate was not hydrogenated with hydrogen introduced into the reaction system of nickel powder and the substrate, but with the dissociated hydrogen generated on the nickel surface in a pretreatment process with hydrogen gas at 200 °C.

Figure 1 also shows that no further increase in the hydrogenation yield was attained with a reaction time longer than 10 min. This finding can be explained by

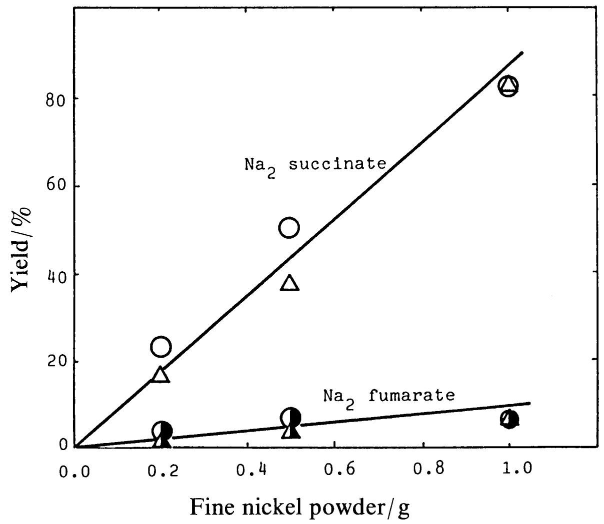

Fig. 2. Dependence of the hydrogenation and isomerization yields on the amount of fine nickel powder. Reaction time: 10 min.
○ ◑: under a H_2 atmosphere,
△ ▲: under an Ar atmosphere.

the following ideas: (1) the molecules in the core area of substrate particles are not hydrogenated, because the dissociated hydrogens cannot reach that area, and (2) the dissociated hydrogens are consumed in the reaction during the first 10 min.

Figure 2 shows the relationship between the amount of fine nickel powder and the hydrogenation yield under either a hydrogen or argon atmosphere. The hydrogenation yield increased linearly with an increase in the amount of fine nickel powder in both cases. This fact supports the second idea that hydrogenation is interrupted because of a lack of dissociated hydrogen in the reaction system.

Additionally, from Figs. 1 and 2 it is observed that not only hydrogenation, but also isomerization of maleate to fumarate, proceeded over fine nickel powder pretreated with hydrogen gas at 200 °C. The isomerization yields change with changes in the reaction time and amount of fine nickel powder in approximately the same profiles as those of the hydrogenation yield versus the reaction time and hydrogenation yield versus the amount of fine nickel powder, respectively. This finding suggests that isomerization was carried out with dissociated hydrogen generated on the nickel powder during its H_2-pretreatment at 200 °C as the hydrogenation.

In summary, it is shown here that hydrogen molecules are dissociated on fine nickel powder at 200 °C and that the dissociated hydrogens are consumed in the hydrogenation of disodium maleate in the solid phase at room temperature. Moreover, the dissociated hydrogens on the nickel powder take part in the isomerization of maleate to fumarate in the solid phase. Further studies on catalytic hydrogenation of organic compounds in the solid phase are now in progress.

Experimental

A typical procedure for the solid-phase hydrogenation and isomerization of disodium maleate is as follows:

Treatment of Fine Nickel Power with Hydrogen Gas. Fine nickel powder with a mean particle size of 20 nm (Vacuum Metallurgical Co., Tokyo) was kept at 200 °C for 0.5 h under flowing hydrogen gas in order to eliminate any oxides on the surface. After cooling to room temperature, the hydrogen-treated nickel powder was subjected to solid-phase reactions of disodium maleate.

Solid Phase Hydrogenation and Isomerization of Disodium Maleate. Hydrogen-treated fine nickel powder (the stated amount) and well-pulverized disodium maleate (64 mg) were placed in a 60 ml glass reaction vessel under an argon atmosphere. The argon gas was substituted by hydrogen gas, and the mixture was shaken for the stated period at 30 °C at an initial hydrogen pressure of 9.8×10^4 Pa.

Product Analyses. After the stated period, the reaction mixture was treated with three 10 ml portions of warm water in order to extract the disodium maleate, fumarate, and succinate. After removing the water in vacuo, the extracts were converted to methyl esters with methanol and sulfuric acid in the usual manner. The methyl esters were subjected to GLC analyses (1.1 m long, 3 mm i.d. glass column packed with 5% PEG 20M on Chromosorb W, at 95 °C). The relative amounts of disodium maleate, disodium fumarate and disodium succinate in the crude product were evaluated from the peak areas of methyl maleate (retention time, 10.2 min), methyl fumarate (4.9 min), and methyl succinate (6.4 min).

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