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ISOTOPE EXCHANGE BY TRIBOCHEMICAL REACTION

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Isotope exchange reaction $H_2 + D_2 = 2HD$ occurs at room temperature tribochemically by vibration of SiC. This reaction, which is distinct from thermal reaction, has an induction period at initial stage and the rate of the reaction increases with increasing vibrating time.

In the field of mechanochemistry, so-called tribochemical processes, which play an important part in friction processes, in rubbing processes and in the like on the chemically active solid surface, have been studied in large numbers by Heinicke et al.[1-3] For example, when the quartz particles are impacted against the gold pieces in CO_2 atmosphere, the reaction $Au + CO_2 \longrightarrow Au_2O_3$ occurs.[4] Generally this reaction is hard to occur thermally and the reaction mechanism is so complicated that the quantitative discussion is said to be difficult. For detailed discussion of tribochemical reaction, it is necessary to simplify the parameters related to the reaction and to study the parameter dependence of the reaction systematically. For this reason, the reaction system had to be selected as simple as possible. In this letter, isotope exchange reaction $H_2 + D_2 = 2HD$, as the simplest reaction, was carried out tribochemically by vibration of silicon carbide particle in a gas mixture of hydrogen and deuterium.

The granular SiC (SiC, over 98.5%; C, below 0.2%; SiO_2, below 0.2%; FeO and S, trace amounts) of 0.6 mm dia. was evacuated at 350°C in a pyrex vessel for removal of adsorbed gas. The equimolar mixture of H_2-D_2 gas (300 mmHg) was derived into the reaction vessel and vibrated (amplitude, 10 mm; vib. frequency, 6.7 Hz and 13.3 Hz) at room temperature. The mole fraction of HD in progress of reaction was measured by a mass spectrometer (Hitachi RM-50).

The HD formation curves for a tribochemical reaction at room temperature and a thermochemical reaction at room temperature and 200°C in contact with SiC are drawn in Figure 1. It is found that the exchange reaction scarcely proceeds without vibration at room temperature, while the rate of tribochemical exchange reaction during the mechanical treatment is accelerated at the same temperature. This figure also shows that the tribochemical reaction with 13.3 Hz proceeds more rapidly than with 6.7 Hz and quickly approaches to the equilibrium. It is predicted from the curves of tribochemical reaction that the rate of reaction changes during the vibrational treatment. In the case of the thermal formation of HD at 200°C, a reaction of the first order is observed, whereas under the influence of mechanical treatment the reaction rate is seemed to be dependent on the treatment times, since an induction period at the initial stage of the reaction is observed. Therefore, time dependence of the rate of reaction was investigated when SiC was vibrated

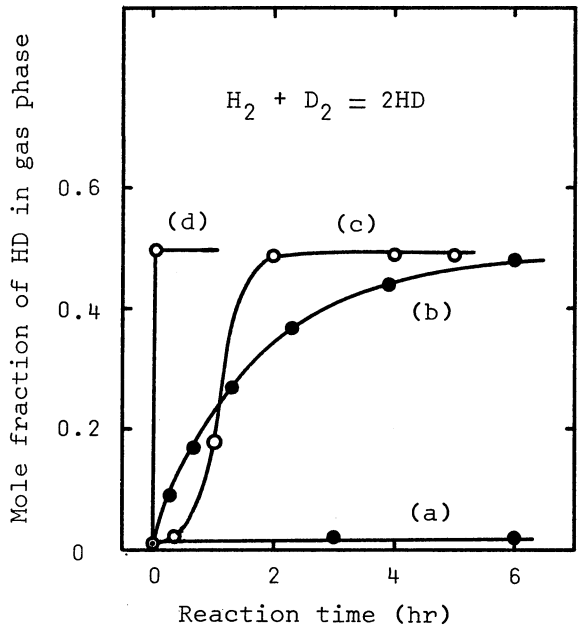

Fig.1. Increase of HD molecules in gas phase with the time of reaction.
Thermochemically, at (a) room temp. and (b) 200°C.
Tribochemically, with (c) 6.7Hz and (d) 13.3Hz.

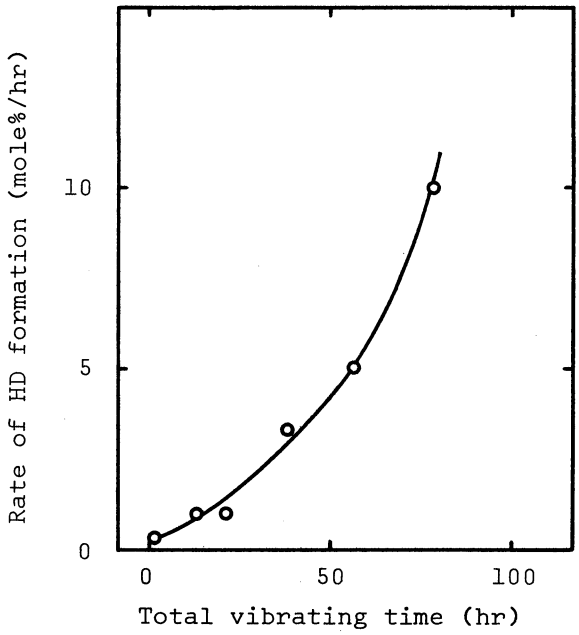

Fig.2. Dependence of the rate of exchange reaction $H_2+D_2=2HD$ on total vibrating time with 6.7Hz.

intermittently. The curve in Figure 2 is shown, with the rate of HD formation after one hour since gas is refreshed as ordinate and with total vibrating times as abscissa. It is ascertained that the longer the vibrating time is, the more rapidly the rate of the reaction by the identical silicon carbide is.

Above experimental results have revealed; 1) the exchange reaction of H_2-D_2 occurs at room temperature by vibrating of SiC, and the larger the vibrating frequency is, the more rapidly the rate of reaction is; 2) there is an induction period at the initial stage of the reaction and the rate of the reaction increases with increasing vibrating time. At first, this reaction is not due to a simple temperature effect caused by frictional heat, because the temperature of SiC does not rise appreciably during vibration, but probably due to an excitation of hydrogen (deuterium) at active sites such as the strain of lattice which is formed by mechanical impact.[5] Then, the increase in the reaction rate with increasing vibrating time is presumed to be due to the increase in the active sites. To clarify this, further experiment must be carried out with the aid of the measurements about the amount of adsorption, the specific surface area, and so on.

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