Conservation of Hydrogen Molecularity in the Hydrogenation of Olefins over Molybdenum Sulphide

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Summary Hydrogen molecularity is conserved in the hydrogenation of olefins and butadiene on molybdenum sulphide, resulting in the [$^2H_2$]-products; the amount of [$^2H_2$]-product was nearly 100% for butadiene, 85% for but-1-ene, *cis*-but-2-ene and propene, and 53% for ethylene.

An interesting feature of the oxide catalysts used in the hydrogenation of olefins is the conservation of hydrogen molecular identity in the products.[1] We now report that a similar conservation of hydrogen molecularity has been observed in the hydrogenation of ethylene, propene, butene and butadiene over molybdenum sulphide. The molybdenum sulphide used in the present experiment has 2H (hexagonal) structure (shown by *X*-ray diffraction) and a surface area of 15 $m^2 g^{-1}$ (BET method with nitrogen adsorbent). The impurities (by atomic absorption analysis) were Fe 0·02, Mg 0·0015, Ca 0·0077, Na 0·012, Mn 0·0003, Cr $< 0·0001$, and K $< 0·1\%$.

Table. The hydrogenation of butadiene with D_2 and with an equilibrated isotopic mixture at room temperature

Conversion/%		35·0	20·0
Hydrogen used/%	H_2	0	73·0
	HD	0	24·7
	D_2	100	2·3
Deuterium distribution of but-1-ene/%	$^2H_0$	0·6	75·0
	$^2H_1$	6·7	22·3
	$^2H_2$	80·8	2·2
	$^2H_3$	10·0	—

The reaction of butadiene with D_2 on MoS_2 at room temperature gave [$^2H_2$]-but-1-ene selectively as shown in the Figure, and its microwave spectroscopic analysis confirmed the formation of 100% 3,4-[$^2H_2$]-but-1-ene. The decrease in the [$^2H_2$]-but-1-ene fraction at higher hydrogenation conversions (Figure) is due to the decrease in D_2 content by the exchange reaction between D_2 and butadiene. The distribution of but-1-enes obtained in hydrogenation with isotopic equilibrated hydrogen is shown in the Table, where [$^2H_0$]-, [$^2H_1$]-, and [$^2H_2$]-but-1-enes are formed according to the gas phase hydrogen composition.

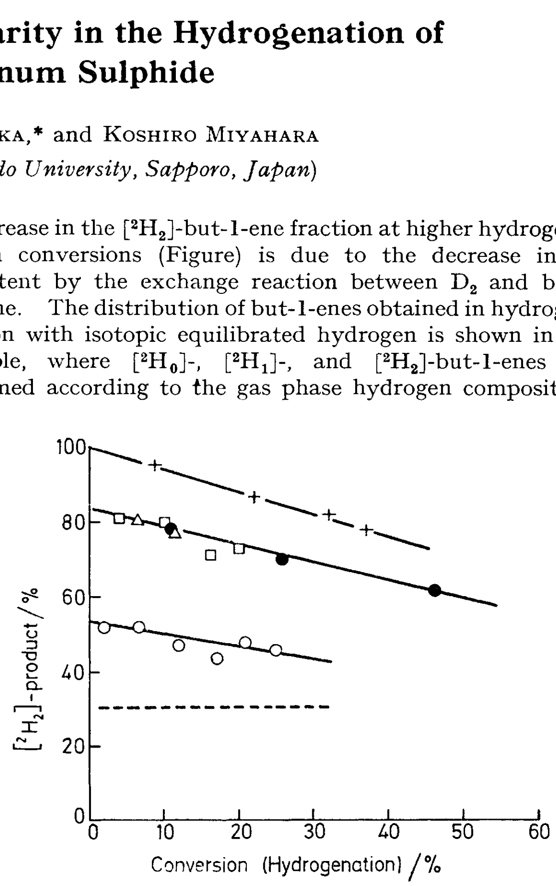

Figure. The fraction of [$^2H_2$]-product in the reaction of D_2 with butadiene (+), but-1-ene (△), *cis*-but-2-eene (□), and propene (●) at room temperature, and ethylene (○) at 0 °C. Dotted line indicates the estimated value of [$^2H_2$]-ethane at random distribution.

The hydrogen molecular identity is conserved nearly 100% in the hydrogenation of butadiene, but for olefins the conservation is lower and there is no distinguishable differences between propene, but-1-ene and *cis*-but-2-ene. Ethylene is especially poor in the conservation of hydrogen molecular identity, but the [$^2H_2$]-ethane shown in the Figure is evidently higher than the value estimated from the random distribution (dotted line), suggesting that there is conservation of hydrogen molecular identity to some extent.

In conformity with the orbital symmetry rule,[2] the molecular addition of hydrogen to the π-bond of olefins or of butadiene seems to be unfavourable. The microwave spectroscopic determination of the D-atom position in the [$^2H_1$]-butadiene molecule has clearly shown stepwise addition *via* the *iso*-butenyl intermediate, $\mathrm{Me{-}\underset{|}{CH}{-}CH{=}CH_2}$.[3] If the hydrogenation of olefins is also brought about *via* this stepwise hydrogen addition, the intermediate in the hydrogenation of but-2-ene should be the isobutyl form, $\mathrm{Me{-}\underset{|}{CH}{-}CH_2{-}Me}$. But-1-ene and propene have two probable half-hydrogenated intermediates, the n-alkyl and isoalkyl forms, but ethylene has only the n-alkyl form.

Thus it is interesting that no appreciable differences can be seen between but-1-ene, but-2-ene and propene, and that only ethylene is rather poor in the conservation.

The existence of two kinds of active sites on MoS_2 has been demonstrated; one is only effective for the isotopic mixing or the isomerization of olefins, and the other is effective for the hydrogenation reaction.[4] In microwave spectroscopic studies of the isotopic mixing of olefins, both the n-butyl and the isobutyl intermediates are formed on the active sites for the exchange reaction, and the n-butyl intermediate is more predominant for the exchange reaction.[5] If the isoalkyl intermediate is the preferable form for hydrogenation, the trend of conservation of hydrogen molecular identity shown by our results can be explained.

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[2] R. G. Pearson, *J. Amer. Chem. Soc.*, 1972, **94**, 8287.

[3] Unpublished work.

[4] T. Okuhara, K. Tanaka, and K. Miyahara, 37th Catalysis Society Meeting, Fukuoka, Oct. 1975.

[5] Unpublished data.