

## Buta-1,3-diene Hydrogenation on a Deuterium Sulphide-treated Molybdenum Disulphide Catalyst

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Deuterium, introduced as  $D_2S$  to a molybdenum disulphide catalyst, has been found to exchange with gas-phase hydrogen and to be incorporated into hydrocarbon products when buta-1,3-diene is hydrogenated on the catalyst; evidence is presented for the participation of hydrogen present on the surface as SH groups.

Interest in the use of molybdenum disulphide as a hydrodesulphurisation catalyst has led to extensive studies of olefin hydrogenation reactions on  $MoS_2$  catalysts, which have recently been reviewed.<sup>1</sup> Mechanisms have been proposed on the basis of the degree of co-ordinative unsaturation of molybdenum similar to the model proposed by Siegel<sup>2</sup> for transition-metal oxide catalysts. Hydrogen sulphide treatment of the catalyst has produced evidence for two types of active sites, one type active for ethylene hydrogenation and the other for ethylene and hydrogen isotopic exchange reactions, and these results have been explained in terms of a diminution of the co-ordinative unsaturation of the molybdenum by the adsorption of hydrogen sulphide.<sup>3,4</sup>

To obtain some insight into the location of the reactive hydrogen on hydrogen sulphide-treated  $MoS_2$  catalysts, we have studied the interaction of butadiene and butadiene-hydrogen mixtures with deuterium sulphide adsorbed on  $MoS_2$ .

Molybdenum disulphide was prepared by thermal decomposition of ammonium thiomolybdate. The ammonium thiomolybdate was precipitated when hydrogen sulphide was passed into ammonium molybdate (0.09 mol) in aqueous ammonia solution (36% w/w; 400 ml) at 65 °C. After being filtered off and dried for 48 h, the ammonium thiomolybdate was decomposed at 1000 °C in flowing oxygen-free nitrogen for 5 h. Electron diffraction showed it to have the molybdenite,  $MoS_2$ , structure. Deuterium sulphide (74.0%  $D_2S$ , 11.8% HDS, and 14.2%  $H_2S$  by mass spectrometry) was prepared by reaction between zinc sulphide (B.D.H.) and  $D_2SO_4$  (Merck, Sharp and Dohme) diluted with  $D_2O$  (Norsk-Hydro).

(i) Isotopic exchange between gas-phase hydrogen and adsorbed  $D_2S$ . Two experiments, each using 0.489 g of  $MoS_2$  catalyst, were performed in which a sample of ' $D_2S$ ' (i.e. the  $D_2S$ , HDS,  $H_2S$  mixture as specified above) was allowed to be adsorbed at 350 °C. The catalyst vessel was evacuated and a measured quantity of hydrogen was admitted. After 40 min the isotopic composition of the hydrogen was determined using a V.G. model MM 601 mass spectrometer. The results are shown in Table 1. The observed deuterium recovery was determined having regard to the isotopic composition of the ' $D_2S$ '; the calculated deuterium recovery was that expected if the deuterium became uniformly distributed between the adsorbed hydrogen sulphide and gas-phase hydrogen. The results show that there is probably complete isotopic exchange at 350 °C, although this claim is subject to uncertainty arising from the isotope effect, which appears to be in favour of deuterium in gas-phase  $H_2$ .

Table 1. Hydrogen exchange with adsorbed  $D_2S$  on  $MoS_2$ .

Expt.	Adsorbed $D_2S$ / $\mu$ mol	$H_2$ for exchange/ $\mu$ mol	Product distribution			%D recovery	
			$H_2$	HD	$D_2$	obs.	calc.
(a)	37.0	39.6	34.0	47.1	18.9	56.9	51.7
(b)	34.1	35.2	26.0	53.4	20.6	58.3	50.8

(ii) Interaction of buta-1,3-diene and adsorbed  $D_2S$ . ' $D_2S$ ' (13.6  $\mu$ mol, equivalent to 21.7  $\mu$ mol of D atoms) was allowed to be completely adsorbed by a fresh sample of  $MoS_2$  at 350 °C. Buta-1,3-diene (33.5  $\mu$ mol) was admitted and the system left for 24 h. Products were separated by gas chromatography using a 12 m column of 33% w/w dimethylsulpholane on 80-60 mesh firebrick. Separated hydrocarbons were isolated in liquid nitrogen-cooled traps and transferred to a mass spectrometer, where they were found to have the deuterium distributions in Table 2. The recovery of deuterium in the products was 9.27  $\mu$ mol of D atoms, which was equivalent to 42.7% of the deuterium introduced as ' $D_2S$ '. Similar experiments with butadiene contact times of 40 min and 6 h showed negligible amounts of butene products and a very small incorporation of deuterium into butadiene, which we therefore conclude to be a very slow process under these conditions.

(iii) Interaction of a 1:3 buta-1,3-diene-hydrogen mixture with adsorbed  $D_2S$ . To investigate the behaviour of deuterium, introduced as  $D_2S$ , under hydrogenation conditions, ' $D_2S$ ' (22.9  $\mu$ mol, equivalent to 36.6  $\mu$ mol of D atoms) was allowed to be adsorbed by a similar sample of  $MoS_2$ . A mixture of buta-1,3-diene (34.2  $\mu$ mol) and hydrogen (103.7  $\mu$ mol) was admitted, and hydrogenation at 350 °C allowed to proceed to 82% reaction (about 80 min). Table 3 shows the results. 23.5  $\mu$ mol of D atoms (64.2% of the deuterium introduced as ' $D_2S$ ') appeared in hydrocarbons. The amount present in the excess of hydrogen was not determined.

From these results it can readily be seen that 41% of the added 'hydrogen' to form butenes from butadiene consisted of deuterium. If the deuterium introduced to the catalyst as ' $D_2S$ ' had first equilibrated with gas-phase hydrogen which subsequently hydrogenated the butadiene, the expected deuterium content of the butenes would have been only 14%. Accordingly we believe that the deuterium is incorporated into hydrocarbons directly from the adsorbed state of the  $D_2S$ , and not *via* the gas-phase hydrogen.

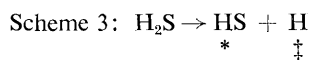
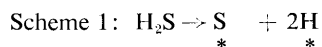
Table 2. Product yields and deuterium distributions from the interaction of buta-1,3-diene with  $D_2S$  adsorbed on  $MoS_2$ .

	Yield (%)	Deuterium distributions (%)				
		$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_{1-8}$
n-Butane	0	—	—	—	—	—
But-1-ene	8.8	63.9	29.4	6.7	0.0	0.0
<i>trans</i> -But-2-ene	33.3	65.1	28.2	5.8	0.8	0.0
<i>cis</i> -But-2-ene	8.6	65.1	28.2	5.8	1.0	0.0
Buta-1,3-diene	49.3	91.5	5.3	2.4	0.8	0.0

Table 3. Buta-1,3-diene hydrogenation on a  $MoS_2$  catalyst pretreated with  $D_2S$ .

	Yield (%)	Deuterium distribution (%)					
		$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	$^2H_{5-8}$
n-Butane	0	—	—	—	—	—	—
But-1-ene	21.3	49.5	5.2	17.0	17.7	10.7	0.0
<i>trans</i> -But-2-ene	30.8	73.2	22.9	3.5	0.4	0.0	0.0
<i>cis</i> -But-2-ene	29.7	72.3	23.7	3.7	0.3	0.0	0.0
Buta-1,3-diene	18.2	97.1	0.4	2.1	0.3	0.0	0.0

We now consider three possible modes of adsorption of hydrogen sulphide on MoS<sub>2</sub> (where \* indicates a bond to a surface molybdenum atom, and ‡ to a surface sulphur atom).



(Scheme 3 corresponds to two identical SH groups chemisorbed to molybdenum.)

Scheme 1 requires three contiguous adsorption sites, so would occur only on type C<sup>3</sup> or <sup>3</sup>M<sup>5</sup> sites, which are assumed to be relatively rare compared to type B (<sup>2</sup>M) sites.<sup>4</sup> We have found H<sub>2</sub>S uptake on MoS<sub>2</sub> (140 μmol of H<sub>2</sub>S g<sup>-1</sup> of MoS<sub>2</sub>) to be greater than that of hydrogen (54 μmol of H<sub>2</sub> g<sup>-1</sup> of MoS<sub>2</sub>), and since hydrogen adsorption would presumably be possible on sites B and C we reject Scheme 1 as the major adsorption mode. Schemes 2 and 3 both involve hydrogen adsorption as SH groups, and there is independent evidence for this from inelastic neutron scattering.<sup>6,7</sup> Kieran and Kemball,<sup>8</sup> in a study of ethanethiol exchange with deuterium on MoS<sub>2</sub>, have found that a greater proportion of the reactive hydrogen comes from the dissociative adsorption of ethanethiol than from H<sub>2</sub> (or D<sub>2</sub>) molecules. This is further evidence that

surface species containing S-H bonds, although derived from a different source, are participating in the surface reaction.

It is concluded that this hydrogen of the SH groups is active in the hydrogenation of buta-1,3-diene. When contrasted with the results of the interaction of butadiene alone with D<sub>2</sub>S, it would appear that the presence of gas-phase hydrogen is necessary in some way to replenish the active hydrogen in the SH groups.

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