Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 114 (2006) 377–382

CATALYSIS TODAY

www.elsevier.com/locate/cattod

D-tracer study of butadiene hydrogenation and tetrahydrothiophen hydrodesulphurisation catalysed by Co_9S_8

Robert C. Hoodless, Richard B. Moyes *, Peter B. Wells **

Department of Chemistry, University of Hull, Hull HU6 7RX, UK

Abstract

H_2/D_2 exchange (473–583 K), 1,3-butadiene hydrogenation (418–513 K) and tetrahydrothiophen hydrodesulphurisation (428–557 K) have been studied over powdered Co_9S_8 (surface area, 7 $m^2\ g^{-1}$) using D_2 as an isotopic tracer. Hydrogen exchange proceeded as a first order process at a modest rate ($k_{540} = 1.0\ h^{-1}\ m^{-2}$) with an apparent activation energy of 67 kJ mol^{-1}. Butadiene hydrogenation was diagnostic as to the surface state of Co_9S_8; samples showed either predominant 1:2-addition or 1:4-addition of hydrogen, interpreted as indicating the presence in the surface of single sites or pair/ensemble sites, respectively. Reactions at 473 K in the presence of D_2 gave butenes containing 0–6 D-atoms: exchange patterns obtained from these D-distributions showed that a proportion of butadiene molecules underwent extensive dehydrogenation during the normal progress of hydrogenation. At 633 K this dehydrogenation activity was evident as self-hydrogenation which occurred in the absence of D_2. Tetrahydrothiophen was desulphurised in the presence of D_2 to thiophen (void of D), butadiene (containing 0–5 D-atoms) and 1-butene (containing mostly 0 and 4 D-atoms). Increase in temperature or in deuterium pressure favoured butene formation so that it became the dominant product (88%). Tetrahydrothiophen also underwent self-hydrodesulphurisation in the absence of D_2. A mechanism is proposed, consistent with this D-tracer information, that accommodates dehydrogenation, desulphurisation and hydrogenation steps in the overall process. The activity of powdered Co_9S_8 exceeded that of powdered MoS_2.

Keywords: Co_9S_8; Hydrogen–deuterium exchange; Butadiene hydrogenation; Tetrahydrothiophen hydrodesulphurisation; D-tracer studies; Dehydrogenation processes

1. Introduction

Hydrodesulphurisation is catalysed by sulphides of Mo, W, Co and Ni, both separately and in combination [1,2] and models have been proposed to interpret the synergy observed in the Co–Mo and Ni–W systems [1–7]. In the most common catalyst, alumina-supported Co-promoted MoS_2, the Co decorates the edges of the layered crystals of MoS_2 [3] (probably the principal active phase) or it may be present as Co_9S_8. As Co_9S_8 it may be involved in contact synergy with MoS_2 [4–6]. However, Co_9S_8 as a pure material has an activity for hydrogenation and hydrodesulphurisation.

Co_9S_8 is isomorphous with pentlandite [8,9]. The unit cell has the formula $Co_{36}S_{32}$ and contains a cubic close-packed arrangement of sulphide ions containing 64 tetrahedral holes and 32 octahedral holes. Of the 64 tetrahedral holes, 32 are occupied by Co^{2+} ions, these being distributed through the lattice in groups of eight which lie at the corners of sub-cubes of edge length 0.250 nm. This distance is similar to the nearest neighbour distance in cobalt metal which is 0.251 nm. Considerable orbital overlap between these ions contributes to the electronic [10], magnetic [11,12], and metallic [13] properties of Co_9S_8. Of the 32 octahedral holes, 28 are pseudo-octahedral, distorted, and empty, whereas four are truly octahedral and each contains a Co atom in a formally zero oxidation state. Thus the solid attains the overall stoichiometry Co_9S_8.

The variability in the unit cell dimensions corresponds to a variation in stoichiometry ranging from $Co_{8.987}S_8$ to $Co_{9.006}S_8$ [14]. Defect diffusivity in Co_9S_8 has been measured [15]. The anion lattice is considered to be nearly perfect and hence

---

Abbreviations: butadiene, 1,3-butadiene; 1-b, 1-butene; *t*-2-b, *trans*-2-butene; *c*-2-b, *cis*-2-butene

* Corresponding author.

** Corresponding author at: Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, UK.

0920-5861/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.cattod.2006.02.078

compositional variations are manifested as an overall deficiency or excess of cobalt. Anion mobility in the lattice is low at moderate temperatures, but cation mobility between octahedral holes is measurable and along grain boundaries can be rapid [16].

According to the phase diagram [17], Co_9S_8 is the thermodynamically stable form of cobalt sulphide under the hydrodesulphurisation conditions used in this work. At 700 K it is stable in H_2/H_2S mixtures containing as little as 0.01% H_2S. The preparative procedure described below, involving use of 9.8% H_2S in H_2, should have provided both a sulphur-rich overall composition and a sulphur-rich surface. Admission of pure D_2 to a reactor containing Co_9S_8 would have resulted in a stable $D_2/D_2S/Co_9S_8$ system after the removal of only 0.1% or so of the surface S^{2-} ions. Reduction to metallic cobalt can only be achieved by passing a continuous stream of pure hydrogen over Co_9S_8.

Hydrodesulphurisation is a complex reaction in which S-atoms are extracted from various molecular environments in feedstock molecules and discharged as hydrogen sulphide [1,2]. Catalyst activity is dependent on the ability of the surface to adsorb the reactants, to activate reactant so as to facilitate C–S bond rupture, to release hydrogen sulphide, and to catalyse the formation of hydrocarbon products. Aspects of these processes are conveniently studied by use of the D-tracer technique which has not previously been applied to reactions over Co_9S_8. Thus, the objectives of the work were, (i) to determine the reactivity of the Co_9S_8 surface towards hydrogen by examination of D_2 adsorption and H_2/D_2 exchange, (ii) to characterise the condition of the surface by examination of the products of 1,3-butadiene hydrogenation, and (iii) to explore the various processes that involve hydrogen during hydrodesulphurisation of tetrahydrothiophen.

In industrial catalysts the sulphide phase is supported on an inert refractory oxide, often alumina [1,2]. In this form the active phase is highly dispersed and often difficult to characterise, so that problems arise in relating activity to surface stoichiometry. In the case of molybdenum sulphide catalysis, we obtained useful information by use of bulk material [18,19], and correspondingly in this investigation of Co_9S_8 the catalyst has been in the form of an unsupported powder. Many novel techniques for the preparation of bulk Co_9S_8 have recently been described [12,20–24]; however, the traditional route involving the sulphidation of Co_3O_4 was used in this investigation.

2. Experimental

Precursor Co_3O_4 was prepared by heating Analar $Co(NO_3)_2{\cdot}6H_2O$ in air for 48 h at 873 K. Six gram samples of Co_9S_8 were prepared in situ by heating Co_3O_4 in a stream of 9.8% H_2S in H_2 for 18 h at 773 K. The structures of both precursor oxide and sulphide catalyst were confirmed by X-ray powder diffraction. The surface areas of samples of Co_9S_8 so prepared were 7 $m^2\,g^{-1}$. Of the various catalyst samples prepared, the two here described typify the two types of behaviour observed.

Reactions were conducted in a static Pyrex reactor attached to a grease-free high vacuum system (background pressure 10^{-6} Torr). Before use tetrahydrothiophen was distilled, butadiene was subjected to several free-thaw cycles, and H_2 and D_2 were each purified by diffusion through a heated Pd–Ag alloy thimble. Deuterium (Prochem) contained 1% HD and no detectable H_2. Reactants were pre-mixed before admission to the reaction vessel; pressures were measured throughout reaction by use of an electronic transducer. All reactions were taken to 100% conversion. Variations of initial rate with reactant pressure and temperature were used to determine orders of reaction and apparent activation energies. Catalytic activities remained constant over substantial periods of use provided reactants were pre-mixed before admission to the vessel. Products were analysed by glc using flame ionisation and flame photometric detection for hydrocarbons and S-compounds, respectively. Mixtures of condensable products were separated into pure components by preparative chromatography before mass spectrometric analysis at 16 eV. Normal corrections were made for the presence of ^{13}C and for ion fragmentation. $H_2/HD/D_2$ mixtures were analysed at 60 eV. Isotope exchange patterns in products (*N*-profiles) were derived from mass spectra by use of Burwell's method [25].

3. Results and discussion

3.1. Hydrogen adsorption and exchange

Deuterium adsorption isotherms were measured for freshly prepared Co_9S_8 at 673 K. Adsorption was slow, equilibration times of 1 h were generally required for the measurement of each point. In a typical isotherm, the extent of adsorption on Co_9S_8-A increased with increasing equilibrium pressure in the range 10–550 Torr and remained constant thereafter up to 900 Torr at a value of 8.6 μmol m^{-2}. Desorption was slow, the isotherms showing hysteresis. The first adsorption was accompanied by the release into the gas phase of some D_2S and 0.5–2 μmol H g^{-1} as HD and H_2. It was expected that freshly prepared Co_9S_8 would be slightly sulphur-rich (see above) so this D_2S formation probably represented removal of excess sulphur from the surface. The HD and H_2 yields represented H-atoms retained from the preparation; this H-release was slow and continued during measurement of the second and subsequent isotherms.

H_2/D_2 exchange ($H_2 + D_2 \rightleftharpoons 2HD$) occurred when 1:1 mixtures were contacted with catalyst at seven temperatures between 473 and 583 K. The reaction obeyed first order kinetics over this temperature range, i.e. the HD yield at time t, $[HD]_t$, was given by the equation $k_t = -\ln(1 - ([HD]_t/[HD]_\infty))$, (e.g. $k = 1.01\ h^{-1}\ m^{-2}$ at 540 K), and the initial rate was first order in total pressure. The apparent activation energy over the range 473–583 K, measured at a constant mixture pressure of 63 Torr, was 67 ± 5 kJ mol^{-1}. The occurrence of exchange demonstrated that sites were present at the catalyst surface where dissociation of H_2 and D_2 molecules and recombination of H and D atoms occurred. The rates were slow by comparison with the very high values typical of reaction over metallic cobalt at these temperatures.

3.2. Butadiene self-hydrogenation

When butadiene was admitted at 633 K to a freshly evacuated Co_9S_8 catalyst in the absence of hydrogen a pressure fall occurred and butenes and butane appeared in the gas phase. The butene composition was: 1-b, 30%; *t*-1-b, 42%; *c*-2-b, 28%, which corresponds closely to the thermodynamic equilibrium composition for this temperature. From a consideration of pressure fall and product formation over several such reactions it was evident that a proportion of butadiene molecules underwent complete dehydrogenation and the H-atoms so released sustained butene and butane formation.

3.3. Reaction of butadiene with D_2

Reactions of butadiene with deuterium at 473 K were catalysed by two samples, Co_9S_8-A and Co_9S_8-B that had previously been used only for D_2 adsorption or isotope exchange studies. Reaction over Co_9S_8-A at 465 K was zero order in butadiene, first order in deuterium, and the apparent activation energy (455–539 K) was 70 kJ mol^{-1}. Catalyst-B was more active than catalyst-A by more than an order of magnitude. The two catalysts behaved differently (Table 1), Co_9S_8-A providing preferential formation of 1-butene, the 2-butene having a low *trans*/*cis* ratio, whereas Co_9S_8-B gave a high yield of *trans*-2-butene and a high *trans*/*cis* ratio.

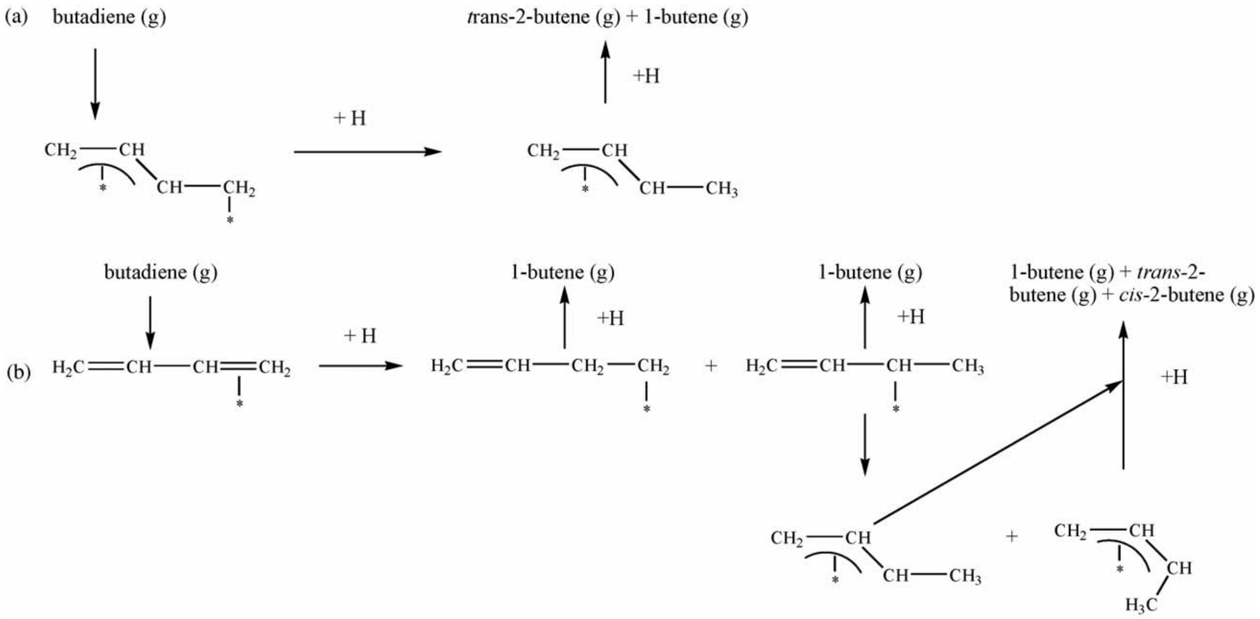
These product compositions provide diagnostic information concerning the nature of the sites on the catalyst surface. Butadiene hydrogenation over metallic cobalt partially poisoned by sulphur provides butene compositions very similar to those shown for Co_9S_8-B in Table 1 [26,27]; indeed high yields of *trans*-2-butene are a common feature of butadiene hydrogenations catalysed by evaporated films of many transition elements after exposure to H_2S [28]. This behaviour has been interpreted to mean [26–29] that pair sites exist at the catalyst surface at which butadiene adsorbs in a transoid conformation (Scheme 1(a)). For butadiene molecules in the gas phase the transoid conformation is the lowest energy state; this conformational preference is retained both on adsorption and on formation of the π-allylic half-hydrogenated state so that, on addition of the second H-atom, *trans*-2-butene and 1-butene are formed as products. The yield of *trans*-2-butene exceeds that of 1-butene because addition of the second H-atom occurs preferentially at the unsubstituted C-atom of the half-hydrogenated state. By contrast, the preferential formation of 1-butene over Co_9S_8-A indicates the existence of single sites in the surface at which butadiene adsorbs by interaction of only one of its π-systems (Scheme 1(b)). Two half-hydrogenated states are formed on addition of the first H-atom, both of which give solely 1-butene on addition of the second. Formation of 2-butene requires rehybridisation of one of the σ-bonded half-hydrogenated states to methyl-π-allylic species (in both *syn* and *anti* conformations) which, on further H-atom addition give all three butenes as products. Evidently, there is no substantial

Table 1
Product compositions in butadiene hydrogenation[a] at 473 K

Catalyst	Conversion (%)	Butene composition (%)			*t*-2-b/*c*-2-b
		1-b	*t*-2-b	*c*-2-b	
Co_9S_8-A	3	70	21	9	2.3
Co_9S_8-A	56	60	26	14	1.9
Co_9S_8-B	11	19	77	4	19.2
Co_9S_8-B	41	21	73	6	12.2
Co_9S_8-B[b]	11	32	61	7	8.7

[a] Initial pressures: butadiene = 30 Torr, D_2 = 60 Torr.

[b] After tetrahydrothiophen hydrodesulphurisation.



Scheme 1.

Table 2
Reaction of butadiene with deuterium over Co_9S_8-A at 473 K[a]: distribution of D in the products and *N*-profiles

Initial D_2 pressure (Torr)	Conversion (%)	Products[b]		Deuterium distributions[c] [$C_4H_{8-x}D_x$ (%)] and *N*-profiles[d] N_x							
				$x = 0$	1	2	3	4	5	6	D.N.
32	8	1-b	D_x	26	23	47	4	tr	0	0	1.29
			N_x	23	0	70	6	1	0	0	
		t-2-b	D_x	19	37	41	3	tr	0	0	1.28
			N_x	11	0	81	7	1	0	0	
		c-2-b	D_x	29	35	34	2	tr	0	0	1.09
			N_x	20	0	72	7	1	0	0	
134	7	1-b		14	24	50	8	2	1	tr	1.61
		t-2-b		9	27	53	8	2	1	tr	1.70
		c-2-b		17	28	43	8	2	1	tr	1.51
418	12	*t*-2-b		8	23	53	12	3	1	tr	1.82

[a] Temperature = 473 K; initial butadiene pressure = 33 Torr.
[b] Butadiene (extracted from each reaction) = 92% C_4H_6; 8% C_4H_5D.
[c] D.N. = Deuterium number = $\Sigma x[C_4H_{8-x}D_x]/100$; tr = trace = 0.1–0.5%; yields of C_4HD_7 = trace or zero.
[d] *a*:*b* = effective D:H = 0.80:1.00 for 1-butene and 0.68:1.00 for 2-butene.

preference for the conformation (*syn* or *anti*) of the π-allylic half-hydrogenated state, and hence the *trans*/*cis* ratio in butene formed by this mechanism is relatively low. Thus, the single preparation procedure described in Section 2 produced surfaces having either a predominance of isolated single sites or a predominance of ensembles of at least two sites; to overcome this variability in surface structure would require the development of more controlled sulphidation procedures for the catalyst preparation stage.

Reaction of butadiene with deuterium over Co_9S_8-A at 473 K gave butenes having a deuterium number (i.e. an average content) of 1.1–1.8 D-atoms per molecule (Table 2). Reactant exchange, producing deuteriated butadiene molecules also occurred. Such reactant exchange causes the pool of D-atoms created on D_2-adsorption to be diluted by H-atoms from the reactant, and this renders difficult the interpretation of the experimental distribution of D in the products. In 1962, Smith and Burwell published a mathematical procedure whereby the experimentally determined distribution of D-atoms in products could be deconvoluted to provide the basic exchange pattern [25]. For butenes formed from butadiene, the procedure permits a product distribution containing 0, 1, 2, 3, . . ., 8 deuterium atoms to be transformed into an *N*-profile in which N_2, N_3, N_4, . . ., N_8 represent the fractions of butene containing 2, 3, 4, . . ., 8 added X-atoms where X = H or D. The calculations involve the ratio *a*:*b* which represents the proportions of D and H in the 'hydrogen' pool on the surface and is a disposable parameter. This procedure was applied to the deuterium distributions shown in Table 2, but no solutions were found which modelled the sharp discontinuity on passing from butene-D_2 to butene-D_3. However, solutions became available if the normal restriction, $N_0 = N_1 = 0$ was lifted, and *N*-profiles of this type are shown in Table 2. The significance of N_0 having a finite value is that this fraction of butene molecules was formed by reaction with a pool of isotopically pure H-atoms, and not by reaction with the mixed H/D pool. Apparently N_0 (typically 20%) constituted the fraction of butene formed at sites where butadiene dehydrogenation occurred, the H-atoms released by such dehydrogenation of some butadiene molecules being consumed in the hydrogenation of others. (This situation has been encountered once before, for butadiene hydrogenation over Au catalysts [30]). The remainder of the butadiene (typically 80%) was formed at sites where such dehydrogenation did not occur. This indicates that H- and D-atom diffusion over the Co_9S_8 surface was sufficiently slow for these two pools of adsorbed 'hydrogen' of different isotopic composition to remain distinct.

Thus, Co_9S_8 possesses single sites and/or pair sites which provide for different interactions of butadiene with the surface, and significant butadiene dehydrogenation activity contributes to reaction under normal hydrogenation conditions.

3.4. Tetrahydrothiophen hydrodesulphurisation

Reactions of tetrahydrothiophen with deuterium were catalysed by Co_9S_8-A (396–545 K) and Co_9S_8-B (428–483 K) following the study of butadiene hydrogenation.

Reactions at 530 K over Co_9S_8-A were of the first order in tetrahydrothiophen and of weakly positive order in deuterium, indicating weak adsorption of both reactants. Values of the apparent activation energies in the region of 120 kJ mol^{-1} were measured over Co_9S_8-A (467–545 K) and Co_9S_8-B (428–483 K).

Primary products under the most mild conditions (396 K, low reactant pressures and conversion) were thiophen, butadiene and 1-butene (Table 3). Co_9S_8-B provided somewhat less thiophen and more butadiene than Co_9S_8-A under comparable conditions. As temperature was raised, 2-butene formation increased at the expense of thiophen. When deuterium pressure was increased butene became the dominant product (Table 4).

Orders of reaction indicate weak adsorption of tetrahydrothiophen but strong adsorption of butadiene; a high surface coverage of butadiene should therefore be established during reaction.

Table 3
Reaction of tetrahydrothiophen with deuterium[a]: effect of temperature on product composition at low conversion

Catalyst	Temperature (K)	Products (%)				
		Thiophen	Butadiene	1-Butene	*t*-2-Butene	*c*-2-Butene
Co_9S_8-A	396	70	12	18	0	0
Co_9S_8-A	415	76	4	16	0	4
Co_9S_8-B	428	50	23	21	4	2
Co_9S_8-A	467	56	8	24	8	4
Co_9S_8-A	474	45	6	35	10	4
Co_9S_8-A	530	12	31	42	11	4
Co_9S_8-A	530[b]	12	62	20	5	1

[a] $C_4H_8S:D_2 = 2:1$; total pressure = 25 ± 5 Torr; conversion = 4–12%.

[b] Self-hydrodesulphurisation (reaction in absence of D_2).

Table 4
Reaction of tetrahydrothiophen with deuterium over Co_9S_8-A: effect of increasing initial deuterium pressure[a]

Initial D_2 (Torr)	Products (%)		
	Thiophen	Butadiene	Σ(Butenes)[b]
10	17	53	30
20	22	32	46
42	14	25	61
60	12	18	70
90	7	13	82
180	4	8	88

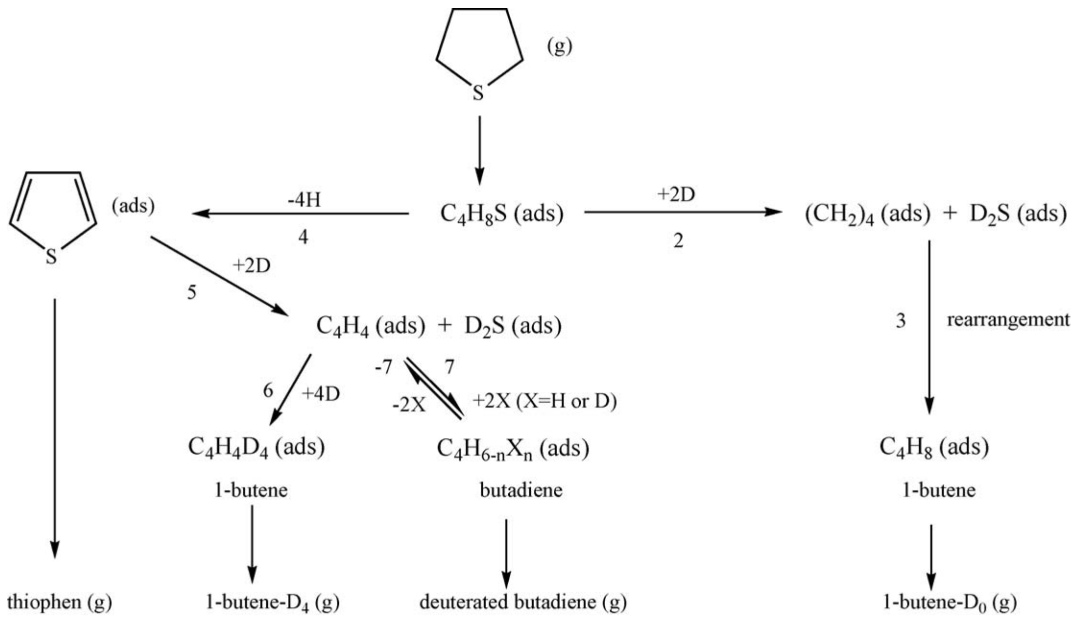
[a] Initial tetrahydrothiophen pressure = 10 Torr; conversion = 25%.

[b] Composition close to: 1-b, 70%; *t*-2-b, 20%; *c*-2-b, 10% throughout.

The D-distribution in the products under low deuterium pressure conditions was remarkably varied. For the reaction shown as entry 5 in Table 3, thiophen contained no deuterium, butadiene contained a wide spread of deuterium ($C_4H_6 = 29\%$, $C_4H_5D = 15\%$, $C_4H_4D_2 = 12\%$, $C_4H_3D_3 = 5\%$, $C_4H_2D_4 = 28\%$, $C_4HD_5 = 11\%$), 1-butene was almost entirely C_4H_8 (68%) and $C_4H_4D_4$ (31%) there being ≤1% of C_4H_7D, $C_4H_6D_2$ and $C_4H_2D_6$ in total. Increasing the initial deuterium pressure from 20 to 100 Torr increased the yield of $C_4H_4D_4$ to 80%.

Immediately after the reaction recorded as entry 5 of Table 1, tetrahydrothiophen was admitted as sole reactant. Self-hydrodesulphurisation occurred at a reduced rate giving more butadiene and less 1-butene in the product.

The mechanism proposed to interpret reaction under mild conditions is shown in Scheme 2. Tetrahydrothiophen adsorption occurs, probably by the interaction of the S-atom at an exposed cobalt site. Depending on the availability or otherwise of adsorbed-D at the adsorption site, so tetrahydrothiophen may undergo either dehydrogenation to thiophen (which desorbs as a primary product) or desulphurisation by reaction with adsorbed-D to form $(CH_2)_4$(ads) which rearranges to 1-butene-D_0 and undergoes desorption as a primary product. Formation of 1-butene-D_4 requires the formation of adsorbed-C_4H_4, which suggests that a proportion of adsorbed thiophen is desulphurised (step 5) and reacts with an isotopically pure pool



Scheme 2.

of D-atoms (step 6) to form 1-butene-D_4. These processes are supported by the observed effect of increasing deuterium pressure which was to diminish thiophen yield (Table 4) and increase 1-butene-D_4 yield.

The origin of butadiene as a primary product is more difficult to assign. That it contains a wide spread of deuterium is indicative of its formation at sites where H/D addition/abstraction (or abstraction/addition) processes of the type $C_4X_n + X \rightleftharpoons C_4X_{n+1}$ or $C_4X_n - X \rightleftharpoons C_4X_{n-1}$ (X = H or D) can occur and where both adsorbed-H and adsorbed-D are available. Such addition/abstraction processes are typical of metal-catalysed reactions [26–29]. This pathway is shown as step 7 in Scheme 2 which is satisfactory only if C_4H_4(ads) is formed in step 5 at two types of site and exhibits two distinct types of reactivity. It is thus proposed that, at 'sulphidic sites' C_4H_4(ads) reacts by successive addition of four adsorbed D-atoms; no addition/abstraction processes occur to dilute the D-pool with H-atoms and cause a redistribution of D thereby reducing the specificity of 1-butene-D_4 formation. By contrast, at 'quasi-metallic sites' C_4H_4(ads) is converted to adsorbed butadiene and H/D addition/abstraction processes occur which provide the wide D-distribution in the product (the norm at metallic surfaces [26]).

As mentioned in Section 1, Co_9S_8 contains 11% of cobalt atoms in a formally zero oxidation state and cobalt atoms/ions possess a degree of mobility in the bulk structure and in the surface. These two states of cobalt may be related to the proposed co-existing sulphidic and quasi-metallic sites. Moreover, this mechanism requires (as did that for butadiene hydrogenation) that H/D-atom diffusion is sufficiently slow for pools of differing isotopic composition to co-exist at the active surface. There is a possibility that the 'quasi-metallic sites' are related to the existence of Co in the zero oxidation state and the 'sulphidic sites' to Co in a positive oxidation state.

Finally, after use for tetrahydrothiophen hydrodesulphurisation, the characteristics of Co_9S_8-B for butadiene hydrogenation were re-examined (Table 1, entry 5). The 1:2-addition character of the catalyst had increased and the 1:4-addition character had diminished. This suggests that hydrodesulphurisation increased the S-content of the surface thereby reducing the concentration of pair sites (and increasing the number of single sites present at the surface) and modifying the butadiene hydrogenation pathways accordingly.

3.5. *Relative activities of Co_9S_8 and MoS_2*

Co_9S_8 powder was an efficient hydrogenation and hydrodesulphurisation catalyst by comparison with MoS_2 [18,19,31]. Its specific activity (i.e. moles reactant converted per second per square metre of surface at a given temperature) for butadiene hydrogenation exceeded that of MoS_2 by an order of magnitude, and for tetrahydrothiophen hydrodesulphurisation, by two orders of magnitude.

4. Conclusions

Co_9S_8 is an active catalyst for H_2/D_2 exchange, butadiene hydrogenation and tetrahydrothiophen hydrodesulphurisation. The surface exhibits varied types of reactivity. In addition to hydrogenation activity it has substantial activity both for C–S and C–H bond fission, the latter contributing to both butadiene hydrogenation and thiophen hydrodesulphurisation. Adsorbed H- and D-atoms have restricted mobility as shown by the coexistence of H/D pools of differing composition in both reactions.

References

[1] R. Prins, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 4, VCH-Wiley, 1997, p. 1908.
[2] H. Topsoe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysis: Science and Technology, Springer, Berlin, 1996.
[3] N.Y. Topsoe, H. Topsoe, J. Catal. 84 (1983) 386.
[4] G. Hagenbach, P. Courty, B. Delmon, J. Catal. 31 (1973) 264.
[5] M. Karroua, P. Grange, B. Delmon, J. Appl. Catal. 50 (1989) L5.
[6] M. Karroua, H. Matralis, P. Grange, B. Delmon, J. Catal. 139 (1993) 371.
[7] R.R. Chianelli, G. Berhault, Catal. Today 53 (1999) 357.
[8] S. Geller, Acta Crystallogr. 15 (1962) 1195.
[9] A.F. Wells, Structural Inorganic Chemistry, Clarendon, Oxford, 1962, p. 526.
[10] H.R. Chauke, D. Hguyen-Manh, P.E. Ngoepe, D.G. Pettifor, S.G. Fries, Phys. Rev. B 66 (2002) 155105/1.
[11] J. Covino, D. Pasquariello, K. Kim, K. Dwight, A. Wold, R.R. Chianelli, Mater. Res. Bull. 17 (1982) 1191.
[12] Y.G. Zhang, F. Guo, Chin. J. Chem. Phys. 17 (2004) 7.
[13] M.G. Townsend, Phys. Status Solidi A 9 (1972) K137.
[14] O. Knopp, M.O. Ibrahim, Can. J. Chem. 39 (1961) 297.
[15] Z. Grzesik, Solid State Ion. 141 (2001) 295.
[16] J.R. Stubbles, PhD Thesis, Imperial College London, 1957.
[17] O. Weisser, S. Landa, Sulphide Catalysts, Their Properties and Applications, Pergamon, Oxford, 1973, p. 48.
[18] M.R. Blake, M. Eyre, R.B. Moyes, P.B. Wells, in: Proceedings of the 7th International Congress on Catalysis, vol. A, 1981, p. 591.
[19] M.R. Blake, M. Eyre, R.B. Moyes, P.B. Wells, Bull. Soc. Chem. Belg. 90 (1981) 1293.
[20] D.M. Pasquariello, R. Kershaw, J.D. Passaretti, K. Dwight, A. Wold, Inorg. Chem. 23 (1984) 872.
[21] X.F. Qian, X.M. Zhang, C. Wang, Y. Xie, Y.T. Qian, Inorg. Chem. 38 (1999) 2621.
[22] J.H. Zhan, X.G. Yang, Y. Xie, D.W. Wang, Y.T. Qian, X.M. Liu, J. Mater. Res. 14 (1999) 4418.
[23] I. Bezverkhy, P. Afanasiev, M. Danot, J. Phys. Chem. B 108 (2004) 7709.
[24] Y.G. Zhang, F. Guo, S.M. Wan, W.W. Zheng, Y.Y. Peng, Bull. Chem. Soc. Jpn. 78 (2005) 277.
[25] G.V. Smith, R.L. Burwell, J. Am. Chem. Soc. 84 (1962) 925.
[26] J.J. Phillipson, P.B. Wells, G.R. Wilson, J. Chem. Soc. A (1969) 1351.
[27] M. George, R.B. Moyes, D. Ramanarao, P.B. Wells, J. Catal. 52 (1978) 486.
[28] A.G. Burden, J. Grant, J. Martos, R.B. Moyes, P.B. Wells, Discuss. Faraday Soc. 72 (1981) 95.
[29] P.B. Wells, in: A.F. Carley, P.R. Davies, G.J. Hutchings, M.S. Spencer (Eds.), Surface Chemistry and Catalysis, Kluwer/Plenum, 2002, p. 295.
[30] P.B. Wells, Acta. Chim. Acad. Sci. Hung. 104 (1980) 134.
[31] R.C. Hoodless, R.B. Moyes, P.B. Wells, Bull. Soc. Chim. Belg. 93 (1984) 673.