

The Influence on Selectivity of the Environment of Catalyst Sites

II. Modification of Cobalt and Nickel Hydrogenation Catalysts by the Action of Sulfur and Other Nonmetals

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The effect of the presence of sulfur on the activity and selectivity of nickel and cobalt powders has been investigated by examination of 1,3-butadiene hydrogenation at 100°C. Nickel and cobalt surfaces devoid of sulfur give preferential 1-butene formation by 1:2 addition (type A behavior), whereas surfaces contaminated by sulfur, in sufficient quantity and suitably incorporated, give preferential 2-butene formation with a high *trans:cis* ratio (type B behavior). Sulfur-contaminated catalysts have been prepared by the reduction of (CoO + CoS) and analogous nickel mixtures, by the adsorption of thiophen and of hydrogen sulfide on nominally clean cobalt powders, and by transfer of sulfur from a contaminated alumina support. The electronic effects on surface sites of sulfur present in an ad-layer and of sulfur incorporated in the surface are distinguishable. Contamination by phosphorus, arsenic, selenium, bromine, and chlorine (but not oxygen) gives type B catalysts similar to those obtained by contamination with sulfur. The effect was not permanent in the case of halogen contamination. This work (i) interprets our previous reports of the existence of "two forms" of nickel and of cobalt, (ii) established 1,3-butadiene hydrogenation as a test reaction for the determination of the extent of contamination of nickel or cobalt catalysts by sulfur and some other nonmetals, and (iii) provides a method for the modification of catalyst selectivity in that the balance of 1:2 and 1:4 addition in 1,3-alkadiene hydrogenation can be controlled.

INTRODUCTION

Previous papers have described "two forms" of nickel and cobalt which differ in their properties as catalysts for diolefin hydrogenation. Type A metal gives preferential 1:2 addition in the hydrogenation of 1,3-butadiene (1) or 1,2-butadiene (2), whereas type B metal gives preferential 1:4 addition in 1,3-butadiene hydrogenation and preferential 1:3 addition in 1,2-

butadiene hydrogenation. Deuterium tracer studies established mechanisms for each type of behavior in each reaction (1, 2). According to these mechanisms, a majority of the half-hydrogenated states in each reaction are chemisorbed as π -allylic intermediates at the type B surface but as σ -bonded and π -olefin bonded intermediates at the type A surface. Over both forms of metal butene isomerization and hydrogenation before desorption are negligible.

A model to interpret the properties of types A and B nickel was presented in 1972 (3). In that study, it was reported that the type of nickel obtained appeared

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to depend on the crystal structure of the oxide from which the metal was formed by reduction. Type A nickel was obtained by reduction of NiO which has the sodium chloride structure, whereas type B nickel was obtained from the layer-structured NiO(OH). The original intention of the present work was to extend the scope of this model by examination of cobalt powders formed by reduction of CoO, CoO(OH), and Co₃O₄. We were curious to know how cobalt prepared from Co₃O₄ would behave, and whether types A and B cobalt could each be prepared in fcc and cph forms.

The present work quickly undermined the model proposed in Ref. (3) and revealed that type B catalysts have contaminated surfaces. In consequence, this investigation became integrated with our other studies of the dependence of catalyst selectivity on the environment of the metal atom site. Thus, Part I deals with the relevance to selectivity of conditions above the site, with particular reference to molecular congestion, Part II (this paper) deals with the effect on contamination in the surface layer, and Part III is concerned with an investigation of the relevance of occluded hydrogen in the bulk of the metal.

The modification of metal catalysts by nonmetals has recently been reviewed (4).

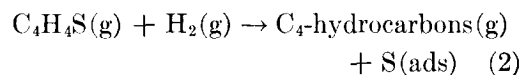
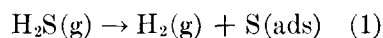
EXPERIMENTAL METHODS

Apparatus, materials, and methods. The apparatus consisted of a conventional grease-free high-vacuum system coupled to a second grease-free system of lower vacuum capability. In the high-vacuum system pressures of 10⁻⁵ Torr or better were attained by a mercury diffusion pump fitted with an efficient liquid air trap and backed by a rotary oil pump. This system incorporated the reaction vessel (130 ml). Pressures in the range of 0.1 to 10⁻⁷ Torr were measured with conventional Pirani and Penning gauges, and those in the range

of 760 to 0.1 Torr with a mercury manometer. The second vacuum system was used to handle gaseous thiophen and hydrogen sulfide and to deliver known doses of these gases to the reaction vessel. It was pumped to 10⁻³ Torr by a two-stage rotary oil pump fitted with a liquid air trap. Pressure of thiophen or hydrogen sulfide (25–10⁻³ Torr) in a known volume was measured using a calibrated LKB thermal conductivity gauge.

Hydrogen was purified by diffusion through a heated palladium–silver alloy thimble. 1,3-Butadiene (Matheson), hydrogen sulfide (Matheson), and thiophen (Koch Light) were degassed carefully before use. All other chemicals were of Analar or equivalent grade; the specified maximum limits of sulfate and chloride in cobalt nitrate and in nickel nitrate were 0.005 and 0.001%, respectively, in each case.

Standard gle methods were used to determine the products of 1,3-butadiene hydrogenation and to ensure that the following dissociations were complete.



Preparations of oxides. The following seven oxides were used in the preparation of cobalt or nickel powder catalysts; the products were shown to be crystallographically pure by X-ray powder photography: 1. CoO was prepared by heating cobaltous carbonate *in vacuo* at 410°C for 17 hr. 2. Co₃O₄ was prepared by heating the hydroxide in air at 950°C for 16 hr and then at 1200°C for 1 hr. The hydroxide had previously been precipitated from a hot solution of cobaltous chloride by sodium hydroxide. 3. Co₃O₄ was also prepared by heating cobaltous nitrate in air at 650°C for 65 hr. 4. CoO(OH) and NiO(OH) were prepared by the methods of Hüttig and Kassler and of Cairns and

Ott (5). A 150-ml solution containing 28 g of potassium hydroxide was added dropwise to a 650-ml solution containing 45 g of cobaltous (or nickel) nitrate and 6 ml of bromine. The precipitated basic oxide was washed and dried. 5. $\text{CoO}(\text{OH})$ was also prepared by the decomposition of cobaltous chlorate solution (6). Equal volumes of cobaltous sulfate solution (56.0 g/liter) and barium chlorate solution (64.4 g/liter) were mixed, the barium sulfate precipitate was removed, and the solution was boiled to dryness whereupon cobalt chlorate decomposed to $\text{CoO}(\text{OH})$, chlorine dioxide, and oxygen. 6. NiO was prepared by heating nickel nitrate in air at 650°C for 67 hr. A commercial nickel oxide (B.D.H.), described by the manufacturers as a nickel (II, III) oxide, was also used; the same material was used in our original work (1, 3).

Metal powder catalysts were prepared from these oxides by heating in flowing hydrogen, or in static hydrogen that was changed frequently. Identical catalytic behavior was obtained with each reduction technique. Each catalyst weighed about 20 mg.

Exposure of metal powders to sulfur compounds was achieved as follows. Known amounts of hydrogen sulfide or of thiophen:hydrogen mixture were expanded into the reaction vessel and retained for a period long enough to ensure complete dissociation according to Eqs. (1) and (2). The minimum time required was a few seconds when surface coverage by sulfur was low, and about 1200 s when the surface coverage was high. Complete dissociation was assured by retaining the dose in contact with the catalyst for 1200 s when the coverage was low and for 3600 s when the coverage was high.

Evaporated metal films were prepared by a standard procedure; 99.9% nickel or cobalt wire was degassed thoroughly before evaporation *in vacuo* onto the walls of a Pyrex vessel maintained at 0°C .

Surface areas of nickel powders were measured by nitrogen adsorption by a one-point BET method (7). The surface area of the cobalt powder was determined by Professor K. S. W. Sing of Brunel University by measurement of the full krypton adsorption isotherm.

Sulfur concentrations in metal powders were determined by radioactivation analysis at the Northern Universities Research Reactor, Risley.

Definitions. A *standard test reaction* was used to determine whether catalysts were of type A or of type B; 50 or 100 Torr of 1,3-butadiene was allowed to react with 100 Torr of hydrogen at 100°C , the products being analyzed after 5–15% conversion. The product composition in this reaction is independent of reactant pressures over a wide range, is independent of conversion until the near removal of butadiene, and is only weakly temperature dependent (1). Catalyst *activity*, plotted in Figs. 1 and 3, represents the initial rate of the standard test reaction expressed in the units of micromoles of butadiene hydrogenated per second per square meter of catalyst sample.

A *good type A cobalt* catalyst provides preferential 1:2 addition, giving a product composition in the test reaction of $80 \pm 5\%$ 1-butene with a *trans:cis* ratio in the 2-butene of about 2.0. A *good type A nickel* gives a somewhat lower 1-butene yield, $60 \pm 5\%$, the *trans:cis* ratio in the 2-butene again being about 2.0. A *good type B* catalyst (Ni or Co) is one which gives preferential 1:4 addition, $75 \pm 5\%$ of the product being 2-butene and $25 \pm 5\%$ 1-butene. An essential characteristic of type B behavior (1) is that the *trans:cis* ratio should be substantially higher than that observed in type A behavior; values are normally in the range 3.5 to 8, and exceptionally as high as 15. Type A catalysts gave butane yields of 0.1–0.5%; type B catalysts gave no butane.

TABLE 1
Behavior of Various Nickel and Cobalt Catalysts in 1,3-Butadiene Hydrogenation

| Form of metal | Precursor | | Reduction temperature ^b (°C) | Catalyst | | Behavior in the test reaction ^a |
|---------------|--------------------------------------|--------------------------|---|----------------|--|--|
| | Formula | Preparation ^a | | Phase | Surface area (m ² g ⁻¹) | |
| Co film | Co wire | | | | | Good type A ^c |
| Co powder | CoO | 1 | 450 | fcc Co | 2.1 | Good type A |
| Co powder | Co ₃ O ₄ | 2 | 450 | (fcc + eph) Co | — | Good type A |
| Co powder | Co ₃ O ₄ | 3 | 600 | fcc Co | — | Good type A |
| Co powder | CoO(OH) | 4 | 450 | fcc Co | — | Good type A |
| | | | 300 | eph Co | — | Good type A |
| Co powder | CoO(OH) | 5 | 450 | fcc Co | — | Good type B |
| | | | 375 | eph Co | — | Good type B |
| Ni film | Ni wire | | | | | Good type A |
| Ni powder | NiO | 6 | 450 | fcc Ni | 0.9 | Good type A |
| | | | 250 | fcc Ni | 2.0 | Good type A |
| Ni powder | Nickel oxide | Commercial | 475 | fcc Ni | 2.8 | Good type B |
| | | | 250 | fcc Ni | 5.7 | Poor type A |
| Ni powder | NiO(OH) | 4 | 450 | fcc Ni | 1.0 | Variable ^d |
| | | | 250 | fcc Ni | 3.1 | Variable ^d |
| Ni powder | NiCl ₂ ·6H ₂ O | Commercial | 450 | fcc Ni | — | Variable ^d |

^a See Experimental Methods.

^b For cobalt powders, 4–5 hr; for nickel powders, 3 hr.

^c Test reaction at 20°C.

^d Catalysts initially good type B but behavior altered with use (see Table 2).

Catalysts giving about equal yields of 1-butene and 2-butene are described as being of *intermediate type*.

The terms *type A*, *type B*, and *intermediate type* are used as adjectives to describe catalysts, surfaces, sites, and product composition.

RESULTS

The Origin of Types A and B Behavior

To test the proposal [Introduction and (3)] that the catalytic behavior of metallic cobalt or nickel is dependent on the crystal structure of the oxide precursor, the oxides described in Experimental Methods were reduced to metal under the conditions shown in Table 1. The evaporated cobalt film and metal powders prepared from CoO, Co₃O₄, and CoO(OH) preparation 4 were each good type A catalysts. This type A behavior was obtained irrespective of the crystal structure of the oxide from which the metal was formed. Thus the model proposed in Ref. (3) founders, and the

experimental results on which it was based require reinterpretation.

However, Table 1 provides clues for the construction of a new model. Of the two preparations of CoO(OH), one (preparation 4) on reduction gave type A cobalt of high activity, whereas the other (preparation 5) gave type B cobalt of relatively low activity. Radioactivation analysis showed that the type B catalyst was contaminated by sulfur (960 ppm by weight); the contamination presumably arose through the use of cobalt sulfate as a starting material in preparation 5.

The behavior of the nickel catalysts (Table 1) supports and extends this interpretation. The evaporated nickel film and the nickel powders formed by reduction of NiO at 250 and 450°C were all of type A and of high activity; the former from its method of preparation is expected to contain no sulfur, the latter cannot have contained more sulfur than that originally present in the NiO (75 ppm by activation analysis). Nickel formed from commercial nickel oxide at 450°C was good type B;

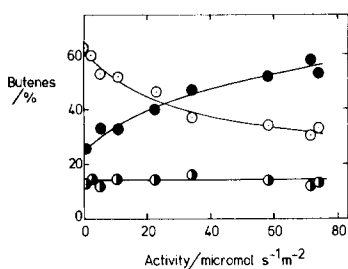


FIG. 1. 1,3-Butadiene hydrogenation at 100°C over various nickel powders. Relationship between butene composition and the activity as measured in the standard test reaction. Filled circles = 1-butene; open circles = *trans*-2-butene; half-filled circles = *cis*-2-butene. For other conditions of the standard test reaction, see text.

activation analysis confirmed the presence of about 350 ppm of sulfur in both the oxide³ and the metal. Thus type B behavior can be induced by the presence of a sufficient level of sulfur contamination.

NiO(OH) preparation 4 gave type B nickel on reduction. This material (like the NiO which gave type A nickel) was prepared from nickel nitrate containing only 50 ppm of sulfur as sulfate. Hence, a more likely nonmetal contaminant than sulfur is bromine, elemental bromine having been used as a reagent in the preparation. Nickel powders produced by reduction of nickel chloride or nickel bromide at 450°C were also good type B (Table 1). Thus, contamination of nickel by halogen also induces 1:4-addition activity.

The observation that CoO(OH) preparation 4 gave type A cobalt on reduction is attributed to an absence of bromine contamination in this case.

Table 1 also shows that the behavior of cobalt is not related to its crystal structure, since both fcc and cph metal gave type A and type B catalysts.

The kinetics of butadiene hydrogenation were examined in detail using the six nickel powders derived from oxides (Table 1).

³ Reference (1) records that a commercial cobalt oxide also gave type B catalysts on reduction above 400°C; this oxide contained 2400 ppm of S.

For both type A and type B reactions the order in hydrogen was 1.3 ± 0.2 and in butadiene -0.8 ± 0.2 at 100°C, and the apparent activation energy (50–150°C) was 52 ± 5 kJ mol⁻¹. Thus, the kinetic form of butadiene hydrogenation is independent of the extent of surface contamination, and the hydrocarbon is adsorbed strongly and hydrogen weakly on both type A and type B surfaces. However, the activities of type A catalysts were higher than those of the contaminated type B catalysts; a smooth dependence of behavior on activity was observed (Fig. 1).

Behavior of Cobalt Catalysts Intentionally Contaminated by Sulfur

The effects of sulfur were examined (i) by contaminating CoO with CoS before reduction and (ii) by chemisorption of thiophen or hydrogen sulfide on clean cobalt catalysts.

Four cobalt powders were prepared by the reduction of (CoO + CoS) mixtures at 450°C for 5 hr. A smooth transition from type A to type B behavior accompanied by a loss of activity occurred as the percentage of CoS originally added to the CoO was increased from 0.0 to 0.9%

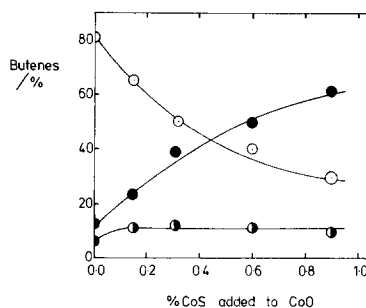


FIG. 2. 1,3-Butadiene hydrogenation at 100°C over various cobalt powders. Variation of butene composition in the test reaction with the percentage of CoS added to CoO before reduction of the resulting mixture at 450°C. Open circles = 1-butene; filled circles = *trans*-2-butene; half-filled circles = *cis*-2-butene. For other conditions of the standard test reaction, see text.

(Fig. 2). Although Fig. 2 confirms that sulfur-contaminated oxides give type B metal on reduction, the reduction temperature is itself of critical importance. A mixture containing 99.2% CoO and 0.8% CoS gave type A catalysts when reduced at 250, 350, and 400°C, but type B catalysts when reduced at 450, 500, and 550°C. [This switch of behavior with reduction temperature was recorded in Ref. (1); as stated above the commercial oxides used in that early work have now been shown to be heavily contaminated by sulfur.] The rapid transition of behavior at about 425°C is now interpreted to be due to a migration of sulfur from the bulk to the surface at this temperature. This was confirmed by reducing one such cobalt powder in a Vacuum Generators ESCA-3 photoelectron spectrometer, and heating the reduced powder in hydrogen over the range of 200–500°C; the S(*2p*) peak first appeared at 425°C. Thus, under these reduction conditions, heavily contaminated surfaces are formed at 450°C and above, whereas at 400°C and below, the surface concentration of sulfur remains at a level below that required for the formation of type B sites (see below).

The formation of type A nickel by the reduction of the commercial (sulfur-contaminated) nickel oxide at 250°C (Table 1) is now interpreted.

An estimate of the amount of sulfur required to form a type B surface was made by observing the effects of the chemisorption of sulfur on 20-mg samples of type A cobalt powder. These powders were taken from a stock prepared by the reduction of CoO at 450°C in flowing hydrogen for 6 hr; their surface area (krypton adsorption) was 2.15 m² g⁻¹. The metallic radius of cobalt being 0.125 nm, the number of atoms in the surface of 1 g of catalyst would be about 3.6×10^{19} on the assumption that mostly low-index planes are exposed. Thiophen or hydrogen sulfide admitted to cobalt was dissociated completely and

hence the ratio of S atoms chemisorbed to Co atoms originally present in the surface, the *S:Co ratio*, is known. This ratio describes the surface conditions provided bulk sulfidation does not occur. As sulfur was deposited on cobalt by thiophen chemisorption at 100°C (Fig. 3a), a linear fall of activity occurred in the range of *S:Co* = 0.0 to 0.25 and this was accompanied by a progressive change from type A behavior to intermediate behavior. No change in activity or in butene composition occurred as the *S:Co* ratio was increased from 0.3 to 0.6. The adsorption of sulfur by hydrogen sulfide chemisorption at 100°C (Fig. 3b) caused a more rapid loss of activity, but the butene composition again showed a linear change to intermediate behavior over the range of *S:Co* = 0.00 to 0.32 and an independence of this ratio thereafter. Type B catalysts were not formed by C₄H₄S or H₂S chemisorption under these conditions at 100°C. However, several catalysts which had achieved intermediate behavior as shown in Figs. 3a and 3b were heated in 200-Torr hydrogen at 450°C for 2 hr. The effect obtained depended on the extent of contamination of the surface of these powders. When *S:Co* = 0.35, the behavior moved back toward type A; when *S:Co* = 0.44 there was no change; when *S:Co* = 0.57, 0.58, or 0.60, the behavior moved to good type B. Hence, the formation of the type B surface requires, *inter alia*, a *S:Co* ratio in the region of 0.55.

In view of the generation of good type B behavior by heating a sufficiently sulfided surface to 450°C in hydrogen, the effect of hydrogen sulfide adsorption at 450°C was investigated (Fig. 3c). The test reactions were, as usual, conducted at 100°C. In this case, the activity diminished slowly, but the catalyst continued to show type A behavior even when *S:Co* = 0.38. At *S:Co* = 0.58, behavior was intermediate, and treatment at 450°C in 200-Torr hydrogen for 2 hr converted the catalyst to the type B state. Thus the presence of a considerable

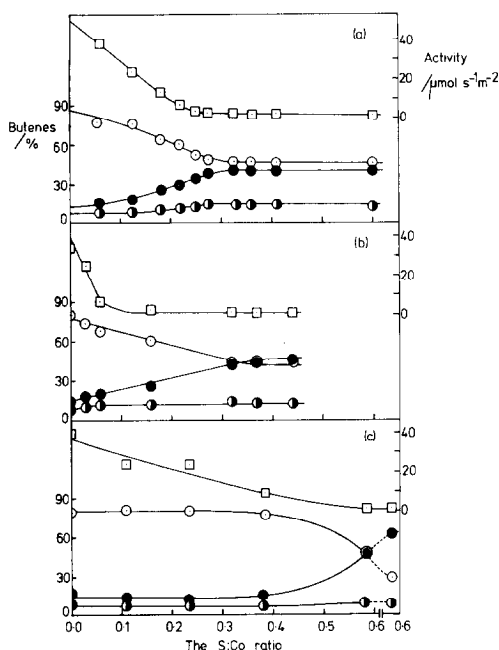


FIG. 3. 1,3-Butadiene hydrogenation catalyzed at 100°C by various clean and sulfided cobalt powders. Variation of activity and of butene composition in the standard test reaction with the value of the S:Co ratio achieved by the chemisorption of (a) thiophen at 100°C; (b) hydrogen sulfide at 100°C; (c) hydrogen sulfide at 450°C. The dashed line in (c) indicates that the catalyst was heated in hydrogen at 450°C. Open circles = 1-butene; filled circles = *trans*-2-butene; half-filled circles = *cis*-2-butene; squares = activity. For other conditions, see text.

hydrogen pressure at 450°C is also essential for the preparation of a good type B surface.

DISCUSSION

We consider here the nature of cobalt and nickel surfaces as their catalytic properties are progressively modified by the action of sulfur. Although we are not concerned with a general description of sulfided surfaces, our model must nevertheless be consistent with the literature concerning the adsorption of sulfur on nickel, the reduction of nickel sulfides, and the catalysis of butadiene hydrogenation by nickel sulfide.

Magnetochemical measurements of hydrogen sulfide chemisorption on nickel-silica at 0 and 115°C indicate that each molecule dissociates completely forming four chemisorption bonds (8). Hydrogen sulfide and methyl mercaptan are chemisorbed on nickel film at -80°C and bulk sulfidation occurs at 0°C after full surface coverage is achieved (9). Nickel catalysts for isoprene hydrogenation have been poisoned with thiophen and a variety of mercaptans; only the surface was sulfided by the action of thiophen at 100°C, whereas sulfidation in depth occurred on exposure to mercaptans at that temperature (10). The rate of bulk sulfidation has been reported to increase with decreasing particle size and with increasing temperature; particles smaller than 40 Å in size are converted to bulk Ni₃S₂ even at -70°C (11). There are two reports of hydrogen sulfide chemisorption at higher temperatures. Richardson reports bulk sulfidation of nickel-kieselguhr by hydrogen sulfide above 300°C (12) and Rostrup-Nielsen describes the monolayer adsorption of hydrogen sulfide on nickel supported on a spinel in the range of 550-645°C (13). In the latter work, reversible adsorption occurred from an (H₂ + H₂S) stream at atmospheric pressure, and the monolayer was complete when the H₂S/H₂ ratio was > 5 × 10⁻⁶; bulk Ni₃S₂ was formed when the ratio exceeded 10⁻³.

Estimates have been made of the ratio of the number of sulfur atoms in a saturated monolayer to the number of nickel atoms in the surface of the clean adsorbent. Rostrup-Nielsen estimates a S:Ni ratio of 0.54 for chemisorption at 550°C, which agrees with the value obtained by Perdereau who made a radioactivity count of ³⁵S chemisorbed on the (100) and (111) planes of nickel (14, 15). Bourne and co-workers (10) propose that random deposition of sulfur on Ni(100) leads at 100°C to incomplete monolayers and calculate S:Ni ratios of 0.19 and 0.38 for thiophen and

mercaptan adsorption, respectively. These lower values arise because an immobile adsorption model was assumed and because it was considered that thiophen requires a site at which the hydrocarbon moiety can chemisorb before sulfur deposition occurs.

The surface structures formed during hydrogen sulfide and thiophen adsorption on low-index planes of nickel have been examined by LEED (16). These structures are loosely packed when exposure is low (14) and more closely packed as exposure increases (15). Some diffraction patterns have been attributed to structures in which sulfur is located between the first and second layers of nickel atoms, the first layer having (100) geometry and the second and subsequent layers (111) geometry (17). It is sufficient, for present purposes, to note that regular structures are indeed formed, and to appreciate that some of the changes in behavior recorded here may be due to the establishment of such structures. However, since type B behavior is a general phenomenon, not confined to sulfur contamination and not dependent upon the establishment of very precise experimental conditions (as is the observation of some LEED patterns), we make no attempt to correlate type B activity with any specific surface structure observed by LEED.

Thermodynamic considerations of the nickel sulfides–nickel–hydrogen system suggest that only Ni_3S_2 , or a mixture of this subsulfide with metallic nickel, is stable under the conditions of catalytic decomposition of heterocyclic compounds in hydrogen at 450°C (18, 19). We discuss our results against this background.

Type A behavior is clearly that provided by polycrystalline nickel or cobalt surfaces which are substantially uncontaminated by sulfur (or certain other nonmetals, see below).

Adsorption of H_2S or thiophen at 100°C in the range of $\text{S}:\text{Co} = 0.00$ to 0.33 was rapid and caused substantial deactivation,

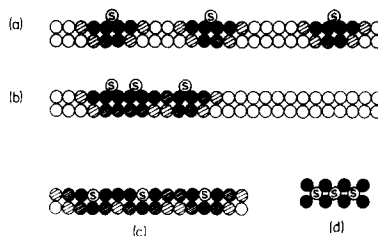


FIG. 4. Diagrammatic representation of the various stages of the proposed interaction of sulfur with nickel or cobalt surfaces: (a) dispersed sulfur atoms in an ad-layer; (b) clustered sulfur atoms in an ad-layer; (c) sulfur atoms incorporated in the surface; (d) formation of a nonstoichiometric subsulfide phase. The degree of shading of the circles representing the metal atoms indicates the extent of the electronic effect of sulfur: unshaded sulfur atoms = type A sites; lightly shaded surface atoms = sites giving intermediate behavior; heavily shaded atoms = type B sites.

and the catalyst changed smoothly from type A to intermediate behavior. Further adsorption in the range of $\text{S}:\text{Co} = 0.33$ – 0.60 was slow, resulted in some reduction of an already low activity, but caused no change in behavior (Fig. 3). It seems reasonable to associate the range of $\text{S}:\text{Co} = 0.00$ – 0.33 with the progressive formation of a layer of adsorbed sulfur atoms which is not close-packed (the model of Bourne *et al.* (10)) and the range of $\text{S}:\text{Co} = 0.33$ – 0.60 with the formation of a progressively more closely packed layer [$\text{S}:\text{Co} = 0.54$ corresponding to the Rostrup–Nielsen model (13)] achieved by slow reorientation so as to accommodate more thiophen (or hydrogen sulfide) and hence more sulfur. The more rapid decay of activity that accompanies H_2S chemisorption (compare Figs. 3a and b) may arise because sulfur deposition, being more random in H_2S chemisorption (10), is more likely to poison the most active sites first.

Sulfur atoms in an incomplete ad-layer will not only obscure surface sites, thus reducing activity by a geometrical effect, but may be expected to modify neighboring sites by an electronic effect. The sulfur–cobalt bond is a polarized covalent bond, i.e., the cobalt atom bonded to sulfur is

polarized $\delta+$. The next-neighbor cobalt atom in the surface will therefore be polarized $\delta\delta+$, and so on (Fig. 4a). These exposed surface cobalt atoms, so polarized, will be better sites for the electron-donating π -allylic intermediates that participate in the type B reaction mechanism (1) than unperturbed surface atoms, and hence the proportion of the reaction proceeding via the type B mechanism will increase with the surface coverage of sulfur when coverage is low. When substantial surface coverage is achieved (S:Co = 0.33), further sulfur adsorption by reorganization of the adsorbed layer should result in no substantial electronic modification of remaining sites, and therefore the product composition should be independent of the S:Co ratio, as observed. However, the progressive reduction in the number of sites as S:Co increases above 0.33 must cause a further reduction in activity, again as observed.

From time to time, poor type A catalysts became of intermediate type, or *vice versa*; these small changes in butene composition were accompanied by changes in activity in the sense expected from Fig. 1. Changes from poor type A to intermediate behavior often accompanied a series of standard test reactions; the reverse change sometimes accompanied an elevation of temperature. We tentatively attribute these changes to a clustering of adsorbed sulfur atoms (movement toward type A; cf. Figs. 4a and b) or to a dispersal of clusters (movement toward intermediate behavior).

The effect of the sulfur ad-layer was sufficient to convert the behavior of catalysts from type A to intermediate, but not to type B. Type B catalysts were formed when surfaces having a S:Co ratio of 0.5 or greater (a saturated surface on the Rostrup-Nielsen model) were heated in hydrogen at 450°C. We propose that, under these conditions, incorporation of sulfur in the surface occurs. Such incorporation may lead to sulfur replacing metal atoms in the surface (Fig. 4c), or to the formation of a

new phase in the surface layer. The new structure, if it resembles any of the conventional subsulfides of cobalt or nickel, will probably be nonstoichiometric since stoichiometric Ni_3S_2 is inactive for butadiene hydrogenation, and Co_9S_8 is inactive at 100°C and shows good type A behavior at 350°C (20). However, such sulfur-deficient structures may possess sulfur atoms in a subsurface layer (shown diagrammatically in Fig. 4d). The atoms of cobalt or nickel in the surface would be (i) of low coordination number and (ii) polarized to an extent signified by $\delta+$, $2\delta+$, or $3\delta+$, depending on the number of sulfur atoms (ions) to which they are coordinated. On *both* grounds, such sites should stabilize the formation of π -allylic intermediates, and be better type B sites than the more mildly polarized sites that give intermediate behavior (Fig. 4a).⁴

We reported above that a catalyst of intermediate behavior having a value of the surface S:Co ratio of 0.35 moved back toward type A behavior on heating to 450°C in 200 Torr of hydrogen. In this case adsorbed sulfur would have become incorporated in the surface forming type B sites of low activity; however, the concentration of sulfur available would have been insufficient to achieve perturbation of all surface cobalt atoms, and hence some reverted to type A behavioral type and high activity.

Finally we interpret the behavior shown in Fig. 3c. The $\text{H}_2\text{S}:\text{H}_2$ pressure ratio that pertained during sulfidation is such that direct formation of a subsulfide is likely (13, 19). The independence of the butene composition on S:Co suggests that patches of stoichiometric subsulfide were formed, and that these were either inactive at 100°C or exhibited type A activity (see above). At S:Co = 0.58 the only sites

⁴The argument that a type B site may be a surface atom of low coordination number was presented in Ref. (3).

TABLE 2
Examples of Nickel Catalysts Showing a Change from Type B Behavior
toward Intermediate Behavior with Use

| Catalyst ^a | Contaminant | Experiment number | Products of butadiene hydrogenation (%) ^b | | | Behavior |
|-----------------------|-------------|-------------------|--|------------------------|----------------------|--------------------|
| | | | 1-butene | <i>trans</i> -2-butene | <i>cis</i> -2-butene | |
| Ni-1 | Br | 3 | 16 | 75 | 8 | Exceptional type B |
| | | 6 | 21 | 67 | 12 | |
| | | 14 | 26 | 62 | 12 | Good type B |
| Ni-2 | Br | 4 | 26 | 61 | 13 | Good type B |
| | | 34 | 36 | 53 | 11 | Poor type B |
| Ni-3 | Br | 3 | 33 | 53 | 14 | Poor type B |
| | | 23 | 44 | 45 | 11 | Intermediate |
| Ni-4 | Cl | 1 | 22 | 66 | 12 | Good type B |
| | | 2 | 28 | 57 | 15 | |
| | | 3 | 30 | 51 | 19 | Poor type B |

^a Ni-1 and Ni-2 weighed 70 mg and were prepared from NiO(OH) preparation 4 by reduction at 450°C. Ni-3 weighed 40 mg and was prepared from NiO(OH) preparation 4 by reduction at 250°C. Ni-4 weighed 40 mg and was prepared from NiCl₂·6H₂O by reduction at 450°C.

^b Standard test reaction at 100°C (see text).

remaining would have been those adjacent to subsulfide patches, and hence modified to give intermediate behavior by the electronic effect described above. Treatment with hydrogen at the same temperature clearly caused considerable modification, probably by labilizing sulfur and

facilitating the following rearrangement: stoichiometric subsulfide + metal → non-stoichiometric subsulfide (Fig. 4d).

Type B catalysts showed a range of activity. Whereas many gave values comparable to those shown in Figs. 1 and 3, we occasionally prepared good type B

TABLE 3
Effects of Contamination of 10% Cobalt-Alumina by 2% Sulfur, Phosphorus, Arsenic, and Selenium, and of Cobalt Powder by 1% Arsenic

| Catalyst | Contaminant ^a | Products of butadiene hydrogenation (%) ^b | | | Behavior |
|------------|--------------------------|--|------------------------|----------------------|------------------|
| | | 1-butene | <i>trans</i> -2-butene | <i>cis</i> -2-butene | |
| Co-alumina | None | 82 | 11 | 7 | Good type A |
| Co-alumina | S | 25 | 62 | 13 | Good type B |
| Co-alumina | P | 25 | 69 | 6 | Very good type B |
| Co-alumina | As | 15 | 70 | 15 | Very good type B |
| Co-alumina | Se | 17 | 64 | 19 | Good type B |
| Co powder | As | 57 | 29 | 14 | Poor type A |
| Co powder | As | 47 | 43 | 10 | Intermediate |

^a Details in text.

^b Standard test reaction at 100°C (see text).

cobalt powders which were more active by at least one order of magnitude. We suspect that our present preparative methods incorporate more sulfur in the surface layer than the minimum necessary for the generation of good type B behavior, and only occasionally and by accident has the optimum surface structure been obtained.

The structure of the sulfur-induced type B site was stable. However, nickel powders which were believed to be contaminated by bromine or chlorine gave type B behavior initially, but quickly moved toward intermediate behavior during successive test reactions (Table 2). Thus, the halogen-induced type B site was not stable.

Contamination of Metal by Impurities Present in the Support

Oliver *et al.* (3) record that a series of nickel-alumina catalysts showed the change from type A to type B behavior with increasing reduction temperature (see above), whereas a corresponding series of nickel-silica catalysts did not. Both series were prepared by impregnation of the supports with the same Analar nickel nitrate that was substantially free of sulfur, and the calcination and reduction procedures were the same in each case. This suggests that the alumina contained a contaminant that was absent from the silica, and that the contaminant was transferred to the supported metal crystallites at 450°C and above, converting their behavior from type A to type B. The Peter Spence type A alumina contained 0.3% sulfate, and hence the participation of sulfur was again suspected. To test this postulate, samples of pure α -alumina (prepared by heating Analar aluminum nitrate at 1050°C for 18 hr) were impregnated with (i) cobalt nitrate or (ii) cobalt nitrate and aluminum sulfate. These materials were each calcined at 650°C, reduced at 450°C, and tested using the standard test reaction at 100°C. Cobalt supported on

pure alumina was type A, whereas cobalt supported on the sulfate-contaminated alumina was good type B (Table 3). Thus contamination of metal by a nonmetal initially present in the support can occur under our catalyst preparation conditions.

This technique has been used to determine whether other contaminants induce type B behavior in cobalt-alumina. The contaminating agents were AlPO_4 to provide phosphorus, Na_3AsO_4 to provide arsenic, and Na_2SeO_4 to provide selenium. The impregnated materials were reduced at 450°C. Table 3 shows that all cobalt catalysts so prepared were good type B. This concurs with a report that nickel phosphate reduced at 650°C shows type B behavior (21).

Elemental arsenic modified the behavior of cobalt. Some 99:1 mixtures of type A cobalt powder and elementary arsenic were heated to 450 and 550°C in hydrogen; the former gave a poor type A behavior in the standard test reaction at 100°C, and the latter intermediate behavior (Table 3). Type B behavior was not obtained.

Attempts to induce type B behavior by oxygen contamination failed.

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