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The Influence on Selectivity of the Environment of Catalyst Sites

III. The Role of Hydrogen Occlusion in Group VIII Metals

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The extent of hydrogen occlusion in powdered Ru, Rh, Os, Ir, Pt, and Au prepared by reduction of the chlorides, and in Co prepared by reduction of the oxide, has been measured by butene titration at 373 K and (except for Co and Ru) by exchange with deuterium. Hydrogen occlusion increased in the sequence Au(= zero) < Co < Pt < Ru < Rh < Os < Ir, iridium attaining stoichiometries in the range $IrH_{0.13}$ to $IrH_{0.20}$. Hydrogen occlusion in iridium was reversible and occurred without expansion of the lattice. The capacity of these metals to occlude hydrogen parallels the extent to which they provide butane when functioning as 1,3-butadiene hydrogenation catalysts. Also, the butane yield varied with the initial hydrogen content of iridium when occluded hydrogen was consumed in hydrogenation. Hydrogen retention is not attributable to normal solution or to the enhancement of solubility by the thermodynamic effects of mechanical stress at defects. Formation of metal from its chloride at temperatures where atomic diffusion is slow leads either to the formation of cavities in which hydrogen is retained, or to the encapsulation of HCl which, under appropriate conditions, reacts with metal to reform chloride and liberate hydrogen (a variant of the Hall model for hydrogen retention in metal formed from oxide). The cavity theory correctly predicts the relative extents of hydrogen occlusion in these metals and hence provides a basis for an interpretation of the general pattern of selectivity shown by the Group VIII metals in the hydrogenation of diunsaturated hydrocarbons that has been recognized for some time.

INTRODUCTION

The two preceding papers of this series show that the selectivity of a metal catalyst may be influenced by molecular congestion at the active site and by the presence of nonmetallic impurities in the surface. The first was purely a geometric effect that influenced the behavior of the adsorbate, and the second was an electronic effect whereby the properties of surface sites were modified. Having thus established that due regard should be paid, when considering the influence of site environment on selectivity, to conditions above and in the surface, attention was turned in this third investigation to the subsurface region and in particular to the role played by hydrogen present in the bulk of the metal. This paper is intended as a preliminary survey.

When alkadienes or alkynes are hydrogenated over Group VIII metals the initial product is usually a mixture of alkene and alkane (*1*). Only in hydrogenations over the Group IB metals copper (*2*) and gold (*3*), and sometimes over the Group VIIB element rhenium (*4*), is alkene the sole product.

When alkane yields obtained under comparable conditions of temperature, reactant pressures, and conversion are

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$$\begin{array}{ccccccc} S_{Fe} & < & S_{Co} & \sim & S_{Ni} & < & S_{Cu} = 1.00 \\ \vee & & \vee & & \wr & & \\ S_{Ru} & & S_{Rh} & & S_{Pd} & & \\ \vee & & \vee & & \vee & & \\ S_{Os} & > & S_{Ir} & < & S_{Pt} & < & S_{Au} = 1.00 \end{array}$$

FIG. 1. The general selectivity pattern. Selectivity, S, of a given metal M, S_M = (total alkene)/(total alkene + alkane).

compared for a wide range of metals, a selectivity pattern is observed. The pattern, which has been examined most exhaustively for the hydrogenation of 1,3-butadiene at subatmospheric pressures catalyzed by supported metals, is given in Fig. 1. Selectivity is observed to diminish as the vertical triads of Group VIII are descended, and to increase from left to right in the first and second transition series. This behavior appears to be substantially independent of the physical form of the catalyst (*1*, *5*).

Selectivities observed in the hydrogenation of ethyne, propadiene, 1,2-butadiene, 2-butyne, and various pentadienes and pentynes, recorded for restricted ranges of metal catalysts, conform to the above pattern (*1*), and hence its generality is well established.

Attention was first drawn to this pattern some years ago, and attempts were made to interpret it in terms of the influence of kinetic and thermodynamic factors on the reaction mechanisms (*1*, *6*, *7*). While these factors may well materially influence selectivity, it is doubtful whether this approach provides an adequate interpretation of this very general behavior pattern.

An alternative model can be conceived in which the origin of the selectivity lies in a physical characteristic of the catalyst rather than in some chemical characteristic of the surface reaction. A hint in support of such a model has been provided by our investigation of the 1,3-butadiene–deuterium reaction catalyzed by rhodium–alumina and by platinum–alumina (*8*). Distributions of deuterium in the butene and in the butane revealed that the latter had been formed at sites where the H availability was higher (and hence the D availability lower) than those at which butene was formed. This suggested that certain regions of the surface were responsible for butane formation, and other regions for butene formation. The present work was undertaken to determine whether such a differentiation of surface regions was related to the phenomenon of hydrogen retention in metals. Metals have been prepared in powder form to obviate support effects and hydrogen spillover.

EXPERIMENTAL METHODS

Preparation of Metal Powders

Stocks of ruthenium, rhodium, osmium, iridium, platinum, and gold powders were prepared by heating the appropriate metal chloride ($RuCl_3$; $RhCl_3 \cdot 3H_2O$; $OsCl_3$; $IrCl_3$; $PtCl_2$; $HAuCl_4$) in a stream of hydrogen at room temperature until the exit gas contained no hydrogen chloride. The temperature was then raised to 473 or 498 K, in increments of 25°, each intermediate temperature being maintained until hydrogen chloride elution ceased. Normally no HCl was formed at 473 or 498 K, and reduction was assumed to be complete. In the case of one iridium powder, gravimetric analysis for chloride confirmed this to be so. Powders were cooled to room temperature in hydrogen. Rhodium and iridium were sometimes pyrophoric, and stocks were stored under nitrogen; the remainder were stored in air. Samples were transferred to static Pyrex reactors of 125-ml volume and heated in 200-Torr hydrogen at 473 or 498 K for 1 hr before use.

A single sample of face-centered cubic cobalt of surface area 2.1 $m^2\ g^{-1}$ was prepared by the reduction of CoO in a stream of hydrogen at 723 K for 6 hr.

TABLE 1

Extents of Hydrogen Occlusion in Some Metal Powders

Method	Temperature (K)	x in MH_x						
		M = Co	Ru	Rh	Os	Ir	Pt	Au
1[a]	293	—	—	0.025	0.11	0.10	0.005	—
1[a]	373	—	—	0.03	—	0.14	—	0.000
2[b]	293	—	—	0.03	—	0.10	—	—
2[b]	373	0.004	0.04	0.02	0.07	0.13[c]	0.007	0.000

[a] Exchange with molecular deuterium.

[b] Butene titration.

[c] Values in this column refer to four samples of a given preparation; values for several preparations ranged from 0.13 to 0.20.

Apparatus

A standard grease-free high vacuum apparatus fitted with mercury diffusion pumps was employed. Butene–butane mixtures were analyzed by glc (*9*), and mixtures of H_2, HD, and D_2 were examined by mass spectrometry.

Measurements of the Extent of Hydrogen Occlusion

Method 1: Hydrogen exchange. Metal powders in the static reactor at 293 or 373 K were pumped to 10^{-5} Torr. Samples of pure deuterium were added sequentially, and each was analyzed on withdrawal. An exchange reaction occurred (except with Au); the first few samples equilibrated in a few seconds or minutes (depending on the metal), but later samples in the sequence required up to 3 days at 373 K to achieve equilibrium. This was interpreted to mean that hydrogen adsorbed at the surface or occluded near the surface exchanged rapidly, whereas hydrogen deep in the bulk required a longer period in which to diffuse to the surface and undergo exchange.

Method 2: Butene titration. Titration of occluded hydrogen with 1-butene was achieved by admission of successive 50-Torr samples of the alkene to an evacuated (10^{-5} Torr) reactor containing the metal powder. No pressure change occurred after butene addition. After an appropriate period, the gaseous hydrocarbon was removed and analyzed. Occluded hydrogen converted 1-butene to butane, and alkene isomerization also occurred. As in method 1, a proportion of the occluded hydrogen was titrated rapidly and the remainder became available for reaction over a more extended period.

RESULTS

Table 1 shows the extent of hydrogen occlusion observed in various metal powders (sample sizes normally about 0.2 g) using methods 1 and 2. Values obtained for the two methods concur. For rhodium, the values obtained at 293 K agree with those for 373 K, whereas for iridium the results for the two temperatures differ significantly indicating that not all of the occluded hydrogen was detected at 293 K.

There is a clear parallelism between the abilities of these metals to occlude hydrogen (as measured at 373 K by method 2) and their selectivities in 1,3-butadiene hydrogenation at 373 K (Fig. 2). The selectivities quoted in this figure are taken from previously published work [Co (*2*); Ru, Rh, Os, Ir, Pt (*9*); Au (*3*)] which utilized alumina-supported metal catalysts. (Experimental conditions, $P_{C_4H_6} = 100$ Torr, temp = 373 K, conversion = 10%.)

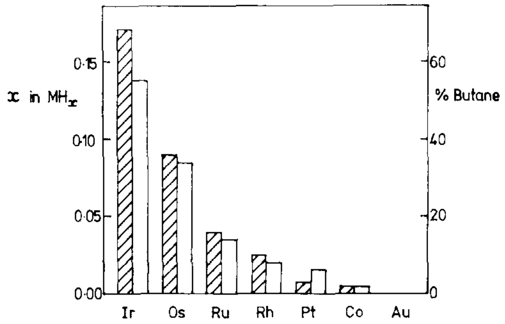

FIG. 2. Comparison of the extent of hydrogen occlusion in metal powders measured by butene titration at 373 K (left-hand ordinate, shaded columns) with the yields of butane, in 1,3-butadiene hydrogenation over metal–aluminas at 373 K (*2*, *3*, *9*) (right hand-ordinate, open columns).

Figure 2 shows that the metals that occlude most hydrogen during their preparation provide the most butane when used as 1,3-butadiene hydrogenation catalysts, and vice versa.

If this parallelism of behavior is genuine and not fortuitous, it is to be expected that the selectivity exhibited by *a given metal* should vary with the extent of hydrogen occlusion. This was tested by preparing samples of iridium with various extents of hydrogen occlusion and examining the selectivities of these samples in 1,3-butadiene hydrogenation. First, a stock of iridium powder having the composition $IrH_{0.17}$ was prepared and divided to provide a dozen or so samples. Each sample was activated in the usual way, and sufficient propene was admitted at 373 K to reduce the extent of hydrogen occlusion from 0.17 to some lower value by consumption of the hydrogen in propene hydrogenation. An excess of 1,3-butadiene was then admitted (the temperature still being 373 K), and the remaining occluded hydrogen was consumed in butadiene hydrogenation. Subsequent glc analysis (i) confirmed that complete conversion of propene to propane had occurred in the preconditioning step, and (ii) provided a value for the selectivity in butadiene hydrogenation. Table 2 shows that the selectivity of iridium does indeed vary with the extent of hydrogen occlusion in the sense expected from Fig. 1. (It should be noted that, as a result of the effect being demonstrated, selectivity varied as the occluded hydrogen was consumed; the selectivities quoted in Table 2 are thus "averaged" values and are necessarily higher than the value quoted in Fig. 1.)

A single experiment using iridium–alumina provided a result in general agreement with those obtained using powdered iridium (Table 2).

DISCUSSION

Part 1. Models for the Occlusion Process

The two titration techniques used in this work measure *both* residual hydrogen chemisorbed at the external surface of the metal particles *and* hydrogen contained in the bulk of the metal (after its diffusion to the surface). Simple chemisorption is unlikely to contribute more than 0.001 to the values of x in MH_x recorded in Table 1. (This value would be attained if one-tenth of a monolayer of chemisorbed hydrogen remained, after the pumping procedure, on the surface of particles 1000 Å in size.) Thus, where x in MH_x exceeds 0.01 (Ru, Rh, Os, Ir) the titrations measure, almost exclusively, hydrogen occluded in the subsurface structure of the metal particles. In the case of platinum, about 20% of the hydrogen available was titrated very rapidly and about 80% exchanged over a lengthy period. Thus, the majority of the

TABLE 2

Dependence of Selectivity in 1,3-Butadiene Hydrogenation on the Extent of Hydrogen Occlusion in Iridium Powder and in Iridium–Alumina[a]

x in IrH_x	0.004	0.01	0.02	0.045–0.06[b]	0.08[c]	0.10	0.17
Selectivity	1.00	0.91	0.82	0.74 –0.80[b]	0.76[c]	0.65	0.55

[a] Experimental details in text.

[b] Five sample examined in this range.

[c] 5% iridium supported on α-Al_2O_3.

recorded value ($x = 0.007$) refers to occluded hydrogen. For cobalt, about 60% of the hydrogen was titrated rapidly and 40% slowly, and thus a minor proportion of the recorded value ($x = 0.004$) is attributable to hydrogen occluded deep in the bulk of the metal particles.

The solubilities of hydrogen in well-annealed metal samples are too low, by many orders of magnitude, to account for the measured extent of hydrogen occlusion. For example, solubilities at 473 K, s, obtained by extrapolation of the best modern published data are (g atom of H) (g atom of metal)$^{-1}$: Ru, $s = 10^{-8}$ to 10^{-9} (*10*); Rh, $s = 10^{-5}$ to 10^{-6} (*10*); Ir, $s = 10^{-10}$ (*10*); Pt, $s = 8 \times 10^{-6}$ (*11*). Hydrogen solubility may be enhanced by one or two orders of magnitude at defects (*12*), and this contributes to hydrogen embrittlement of metals and to stress corrosion cracking (*13*). However, such an effect is insufficient to bridge the gap between the hydrogen solubilities quoted above and the extents of hydrogen occlusion measured in this work.

There is an extensive literature concerning hydrogen retention in Raney nickel and slow hydrogen absorption into evaporated nickel films; in the latter case the amount of hydrogen involved may be three orders of magnitude larger than that attributable to solution (*14*). These observations bear on the present work insofar as the two models that have been developed to interpret the observations provide alternatives for our consideration. One view has been that such sorption is a property of the defect structure of the metal, the hydrogen being held in vacancies in the metal structure (*15*); the other view attributes sorption to the presence of impurity oxygen in the bulk of the metal (*16, 17*).

1. The defect structure model. The notion that occluded hydrogen may be contained in cavities is not new. It has long been known that bulk metal can be made to occlude hydrogen by heating above a rather indefinite "opening temperature" under high pressures of hydrogen. Smith (*18*) states that all characteristics of occlusion (particularly its extent and the permeability of the hydrogen involved) "are simply interpreted as resulting from the presence, in the metal lattice, of an expanding and contracting system of voids." Such voids, in his view, were caused by the rifting of metal crystals, for example, by the creation of enlarged interplanar spacings. However, the present work has not involved the generation of occlusive capacity by use of high temperatures and pressures. Therefore the possibility is explored that cavities in solids are formed under the quite different conditions that obtain during catalyst preparation at 473 K.

The mechanism of formation of a metal powder by the reduction of a metal chloride in hydrogen involves: (i) the transport of hydrogen molecules to the chloride; (ii) hydrogenolysis of metal–halogen bonds, which may lead to the formation of unstable hydrido compounds; (iii) reaction of the latter to form metal clusters, probably with hydrogen ligands; (iv) transport of gaseous HCl away from the site of reduction; and (v) growth of clusters to form polycrystalline metal. The degree of crystallinity of the metal powder so produced will depend upon the mobility of the metal atoms formed in the last step, and this mobility will be governed by the reduction temperature. A high degree of crystallinity will result when the rate of diffusion of metal atoms is greater than their rate of formation. Conversely, poor crystallinity will be obtained when the diffusion rate of metal atoms is small in comparison with the rate of formation. The diffusion rate at a given temperature will vary from one metal to another. It is sufficient, for present purposes, to recall the Hüttig and Tammann rules which indicate that self-diffusion in the surface regions and in the bulk of metal specimens become significant at, respectively, one-third and one-half the temperature of the melting point. Remembering that all metal atoms at the moment of their formation are in a surface, we note that, for the catalysts prepared in this work, only in the case of cobalt (mp, 1492 K; reduction temperature, 723 K) was diffusion likely to have been appreciable during reduction. Thus, the crystallites of Ru, Rh, Os, Ir, and Pt are likely to have been highly disordered structures, these disorders consisting in general of multiple vacancies, or cavities, in the structure.

A cavity model is attractive for the interpretation of hydrogen occlusion on the following grounds.

(i) Such cavities provide locations particularly suited for hydrogen storage. In small cavities, e.g., single, double, or triple vacancies, hydrogen atoms may exist as protons at regular lattice points, having given up their electrons to the conduction band of the metal. In large cavities, hydrogen atoms would be chemisorbed to metal atoms bounding the cavity. The attainment of the extents of occlusion of the magnitude observed can be readily envisaged.

(ii) The containment of hydrogen in cavities does not require expansion of the metal lattice. No lattice expansion was observed by X-ray powder photography, even for $IrH_{0.20}$.

(iii) A proportion of the occluded hydrogen was removed rapidly in the butene titrations, showing that its mobility within the metal was high. The rate of diffusion of hydrogen between cavities cannot be assessed without information concerning the concentration and average geometry of the cavities. However, if protons at lattice points were in equilibrium with chemisorbed hydrogen and proton tunneling between adjacent cavities was facile, the whole of the occluded hydrogen would be capable of transport through the metal lattice and of estimation by butene titration or hydrogen exchange.

(iv) The capacity to occlude hydrogen was a permanent physical property of the metals studied; after the removal of occluded hydrogen by titration with butene the original concentration of occluded hydrogen could be reestablished (iridium, 373 K) by exposure of the metal to molecular hydrogen. Thus, the proposed cavities are stable in the absence of hydrogen. This is to be expected on the basis of the model; the cavities, once formed, can only be annihilated by diffusion of metal atoms in the bulk of the crystallites. Since the cavities were formed under conditions where *surface* diffusion was slow, temperatures substantially higher than the reduction temperature would be required to provide sufficiently fast *bulk* diffusion to cause cavity annihilation.

(v) This cavity model predicts that the greater the difference between the Hüttig temperature, T_H, and the reduction temperature, T_R, the greater will be the degree of atomic disorder in the metal, the greater will be the cavity concentration, and hence the greater will be the extent of hydrogen occlusion. Such a trend is indeed observed. The sequence of melting points (or of T_H) is

$$Os > Ir > Ru > Rh > Pt > Co,$$

whereas the sequence of diminishing extent of hydrogen occlusion is:

$$Ir > Os > Ru > Rh > Pt > Co.$$

This variation of the extent of hydrogen occlusion from metal to metal can be predicted quantitatively. Let us assume that the rate coefficient for the creation of cavities during reduction, k, diminishes with increasing temperature according to the equation: $k = A \exp(E/RT)$ and hence that the relation between the rate coefficients at two temperatures is given by Eq. (1).

$$\ln k_1 - \ln k_2 = E(T_2 - T_1)/RT_1T_2 \quad (1)$$

If (a) the temperature coefficient E has the same value for all of the metals studied, (b) the rate coefficient for the creation of cavities at the various Hüttig temperatures is the same for all of the metals studied, (c) the extent of hydrogen occlusion (x in MH_x) is a linear function of the concentration of cavities formed at the reduction temperature, and if this concentration is proportional to k, then [using subscript 1 in equation (1) to denote the reduction temperature, T_R, and subscript 2 the Hüttig temperature, T_H], we have:

$$\ln x = E(T_H - T_R)/RT_HT_R + \text{constant} \quad (2)$$

Figure 3 shows there to be a fair linear correlation between $\ln x$ and $(T_H - T_R)/T_HT_R$ for Pt, Rh, Ru, Ir, and Os, the value of E being ~50 kJ mol^{-1}. Cobalt does not appear in Fig. 3 because, for this metal, T_R exceeds T_H.

2. The impurity encapsulation model. Hall and co-workers have observed that an amount of hydrogen equivalent to 50 monolayers may be reversibly adsorbed at elevated temperatures by copper–nickel alloy powders (*16*). It was subsequently shown (*17*) that water was encapsulated in the metal during reduction of the oxides and that subsequent hydrogen evolution from the metal occurred on reoxidation: $H_2O + Ni \rightarrow NiO + H_2$. Hydrogen absorption occurred by the reverse process. These authors quote other published work in support of their interpretation. Thus it is necessary to consider whether hydrogen occlusion in the present work may have resulted from an analogous encapsulation of HCl during reduction, and from the release of that hydrogen by the process (for iridium): $6HCl + 2Ir \rightarrow 2IrCl_3 + 3H_2$. While this possibility cannot be eliminated without further experiment, the following considerations render it doubtful. First, the preparation of $IrH_{0.20}$ would, on this basis, involve the encapsulation of enough HCl to generate 6.6% $IrCl_3$ on titration of the hydrogen. Reduction would have proceeded 93.4% to completion, whereas gravimetric analysis indicated complete reduction (with 2% experimental uncertainty, assuming the stoichiometry of $IrCl_3$ to be exact). Second, the stepwise temperature profile adopted in the reduction procedure provided the best conditions for thorough reduction. Third, the impurity encapsulation model fails to interpret the relative extents of hydrogen occlusion in the noble Group VIII metals. Last, the selectivity pattern which parallels the pattern of hydrogen occlusion (Fig. 1) and to which it is related (see below) has been observed by many workers who have used various sources of the noble metals in their catalyst preparations. It is doubtful whether incomplete reduction is practized so widely. Nevertheless, it must be admitted that a proper evaluation of this must await a detailed investigation analogous to that conducted by Scholtus and Hall (*17*).

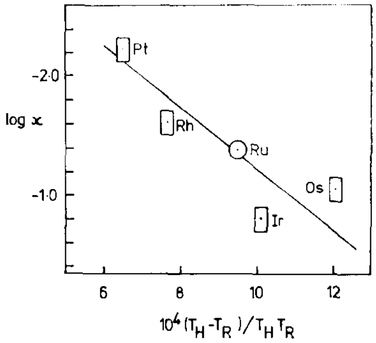

FIG. 3. Rationalization of the extents of hydrogen occlusion in Ru, Rh, Os, Ir, and Pt; evidence that hydrogen occlusion in these metals obeys Eqs. (1) and (2).

Part 2. Hydrogen Occlusion and Selectivity

We turn finally to consider the effect of hydrogen occlusion, whatever its origin, on catalyst selectivity. The two most important experimental observations are, first, that the selectivity, as defined in the Introduction, is a permanent feature of a catalyst throughout its life, and second,

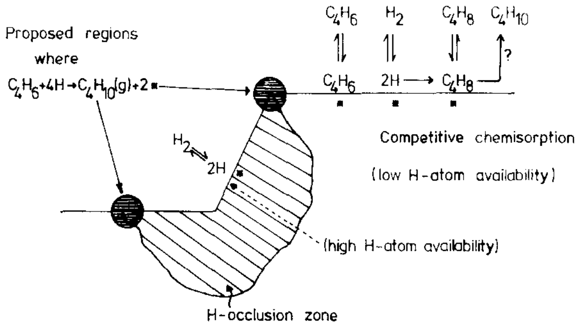

FIG. 4. Schematic representation of a metal consisting of a highly ordered zone (unshaded) and a cavitated zone which occludes hydrogen (lightly shaded), and showing regions of the surface where (i) selective hydrogenation of 1,3-butadiene to butene and (ii) nonselective hydrogenation to butane (heavily shaded) are proposed to occur.

that selectivity parallels the measured extent of hydrogen occlusion in metals (Fig. 2). Consequently, any reaction mechanism for butane formation which involves the participation and consumption of occluded hydrogen in a surface reaction must be accompanied by a mechanism for the rapid replacement of this hydrogen under normal reaction conditions.

Figure 4 shows a cross section through a catalyst particle consisting of a cavitated zone containing occluded hydrogen (shown lightly shaded), and a highly ordered zone (unshaded) where hydrogen concentration in the bulk does not exceed the normal solubility. At the surface of the latter, butadiene and hydrogen chemisorb competitively, the former strongly and the latter weakly, so that a high surface concentration of hydrocarbon reacting with a low surface concentration of chemisorbed hydrogen gives highly selective formation of butene ($S \rightarrow 1.000$, perhaps). The surface of the hydrogen occlusion zone, however, will be a region of intrinsically high hydrogen availability so that, at the junction of the zones, the dark shaded regions in Fig. 4, the hydrogen supply will be sufficient to convert butadiene to butane, giving very low values of selectivity ($S \rightarrow 0.000$, perhaps). Hydrogen consumed from the occlusion zone must be replaced by hydrogen chemisorption and diffusion into the internal cavities as is shown schematically. This requirement for facile chemisorption of hydrogen at the surface of the occlusion zone suggests that butadiene chemisorption at this surface does not achieve high coverage, due perhaps to the disordered arrangement of metal atoms characteristic of this zone. Any butadiene that does undergo chemisorption would be converted to butane.

This model is supported by our published observation (*8*) that, in the reaction of 1,3-butadiene with deuterium catalyzed by rhodium, the pool of 'hydrogen' available for butene formation had an effective protium:deuterium ratio which differed from that available for butane formation. The suggestion was advanced that butene and butane were formed at different regions of the surface; Figure 4 now provides an elaboration of that conclusion.

Implications of the Present Work

A modification of the cavity concentration in a given metal should modify catalyst selectivity. Thus it should be possible to prepare iron, cobalt, or nickel catalysts of low selectivity by preparation of the metal using low temperature methods. Likewise, ruthenium, rhodium, osmium, iridium, and platinum prepared at unusually high temperatures should exhibit selectivities higher than those presently recorded.

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