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Alkene Hydrogenation and Related Reactions

A Comparison of Heterogeneous with Homogeneous Catalysis

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A relationship between the degree of coordinative unsaturation and the set of elementary reactions involving hydrogen and simple alkenes which may occur at a particular reaction site on the surface of a transition metal oxide is proposed. The theory is based upon the mechanisms which best account for the action of two representative homogeneous catalysts, chlorotris(triphenylphosphine)rhodium(I) and hydridocarbonyltris(triphenylphosphine)rhodium(I). The theory is illustrated by reference to reported reactions on cobalt oxide and chromia catalysts.

INTRODUCTION

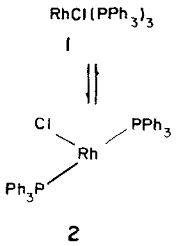
The description of the mechanisms of reactions which are catalyzed by the surfaces of transition metals or their compounds are based increasingly upon knowledge of the chemistry of coordination compounds of these elements (*1–8*). Hypothetical surface complexes are described as analogs of complexes of known structure and their chemical properties are presumed to be related. The elementary reactions used to represent a particular surface catalyzed reaction are often written as analogs of those postulated in known homogeneous catalyzed reactions in which the connection between kinetics and mechanism is relatively direct (*2, 6–8*).

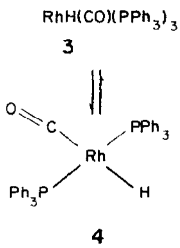
Proposals regarding the atomic arrangement at an active center of the solid catalyst have been advanced; a notable example is given in the treatment of the mechanism of the titanium chloride catalyzed polymerization of ethylene and α-olefins by Cossee and Arlman (*8*). The importance of coordinative unsaturation of the transition metal atom at an active site was emphasized; the location of these sites was deduced from the crystal structure of titanium chloride and arguments concerning the mode of formation of surface defects. The creation and structure of active sites on transition metal oxides and sulfides in general (*3*) or chromia (*9, 10*) and zinc oxide (*7b*) in particular, have also been described.

Coordinative unsaturation is well recognized as a principle structural requirement for catalytic activity (*8, 9, 11–13*). In this paper we will demonstrate a connection between *the degree of coordinative unsaturation* (the number of vacant coordination positions per atom) and the *set of elementary reactions* involving hydrogen and simple alkenes which may occur at a particular reaction site. The elementary reactions are those which seem best able to account for the homogeneous catalyzed hydrogenation and exchange reactions of alkenes and the H_2–D_2 equilibration (*14–16*). In particular we will show how the mechanism of action of two representative homogeneous catalysts can be used to resolve the detailed experimental results obtained by Tanaka, Nihira and Ozaki (*17*) on the hydrogenation and deuterium exchange reactions which occur on cobalt oxide. The same principles will be extended briefly to similar reactions on chromia.

TWO REPRESENTATIVE HOMOGENEOUS CATALYSTS

Chlorotris(triphenylphosphine)rhodium(I), **1**, and hydridocarbonyltris(triphenylphosphine)rhodium(I), **3**, represent two distinctively different types of catalysts. They give rise to different rate laws (*14*, *15*) and stereochemistry (*16*); the H_2–D_2 exchange reaction is catalyzed by **3** but not by **1** (*14a,b*). The structural distinction is clearly evident in the molecular species, **2** and **4**, which are formed by the dissociation of one molecule of triphenylphosphine from **1** and **3**, respectively. Apparently in benzene the degree of dissociation of either **1** or **3** is small (*14c*, *15*, *18*, *19*). The species **2** can associate simultaneously with one molecule of H_2 and one of alkene to form a complex which goes on to alkane through an intramolecular, ligand migration reaction. It does not catalyze the H_2–D_2 equilibration because only three coordination sites are vacant rather than four. Although in principle another ligand might be replaced, this apparently does not occur, presumably because of unfavorable thermodynamics.





In comparison, **4** can associate with one molecule of alkene but not at the same time with an additional molecule of hydrogen until the hydrido ligand migrates to the alkene (*14c*). The latter sequence leads to alkane and regenerates **4**. However in the absence of alkene, the H_2–D_2 exchange occurs rapidly since a molecule of deuterium can add to **4** and the decomposition of the hydridodideutero species can yield HD.

RELATIONSHIP BETWEEN THE CHARACTERISTIC REACTIONS OF 2 AND 4 AND SOME CATALYTIC PROPERTIES OF COBALT OXIDE

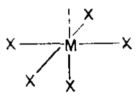
Recently Tanaka, Nihira and Ozaki (*17*) reported on the hydrogenation of ethylene on cobalt oxide. When freshly prepared and activated by heating to 400–450°C, Co_3O_4 is an active hydrogenation catalyst even at −70°C, however the activity drops with use. Treating the fresh catalyst with hydrogen results in the absorption of hydrogen and a decrease in activity although the resulting catalyst is stabilized. The preadsorbed hydrogen does not appear to exchange with gas phase deuterium, however the H_2–D_2 equilibration proceeds rapidly on the stabilized catalyst. Ethylene is adsorbed reversibly and inhibits the H_2–D_2 equilibration. The ethane produced under these conditions results, mainly, from the simple addition of either H_2 or D_2 molecules to ethylene. Some exchange does occur but the amount depends upon the proportion of ethylene in the gas phase.[*] On either fresh or stabilized catalyst, the isotopic exchange reaction between C_2H_4 and C_2D_4 occurs rapidly. However the effect upon the rate of exchange of the pretreatment with hydrogen was not determined.

The above results can be "explained" by reference to the mechanism of catalysis by **1** and **3** as follows:

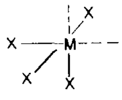
The activation of Co_3O_4 by evacuation at 400–450°C presumably produces coordinatively unsaturated cobalt atoms (*21*). Depending upon their location at the surface, these atoms may be mono-, di-, or tri-coordinatively unsaturated, i.e., they will be able to coordinate with the given number of molecules of monodentate ligands such as carbon monoxide or alkene. The proportion of these sites is a function of the method of preparation of the catalyst. The oxidation state of the cobalt atom is undoubtedly an important variable for its chemical reactivity, and will be assumed to be appropriate for the reactions under consideration (*3*, *8*, *9*, *12*). Accordingly, attention is focused on the consequence that such atoms, which differ in the number of unfilled coordination sites, exist on the surface.

[*] On a platinum catalyst, a mixture of H_2 plus D_2 adds to an alkene as if there is complete mixing of the hydrogen isotopes on the surface of the catalyst before addition to the alkene (*20*).

We will assume that these cobalt atoms reside in formally octahedral surroundings (*8*). The several types of coordinative unsaturation can be represented by structures **A**, **B**, and **C** where X represents an oxygen of the lattice



A



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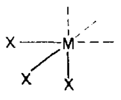


C

and the broken lines indicate vacant coordination sites (*8, 9, 22*). Dowden and Wells (*3*) discussed the possible coordination numbers for the surface sites on ionic solids and metals. They applied crystal field theory to the consideration of the energetics of adsorption on the distorted surface complexes for various changes in coordination number and geometry. Burwell *et al.* have made use of crystal models to describe the formation and geometry of active sites on α-Cr_2O_3. In this work they considered sites corresponding to **A** and **B** but not **C**. All three types of structures were assumed by Selwood (*22*) to be present on chromia catalysts.

We suggest that the above surface structures can be characterized by the reactions each catalyzes. To illustrate we select the following test reactions:

Hydrogen–deuterium equilibration:

$$H_2 + D_2 \rightleftharpoons 2HD. \quad (1)$$

Hydrogenation:

$$H_2 + C_2H_4 \rightarrow C_2H_6. \quad (2)$$

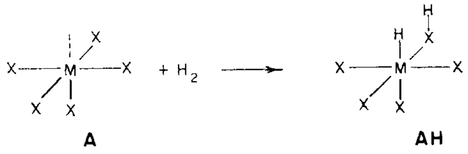
Alkene–deuterium exchange:

$$D_2 + C_2H_4 \rightleftharpoons C_2H_3D + HD. \quad (3)$$

Alkene exchange:

$$C_2H_4 + C_2D_4 \rightleftharpoons C_2H_{4-n}D_n + C_2H_nD_{4-n}. \quad (4)$$

The coordinative unsaturation indicated in types **A**, **B** and **C** can be satisfied by association with CO or alkene. However combination with molecular hydrogen can be brought about in two ways: (a) heterolytic dissociation as in Eq. (5), or (b) insertion (oxidative addition) on sites of types **B** and **C** as in Eq. (6) (*11b*). For H_2–D_2 equilibration to occur, a second pair of coordinatively unsaturated sites must be closely associated with the first, i.e., either two type **A** sites or perhaps a type **B** site:



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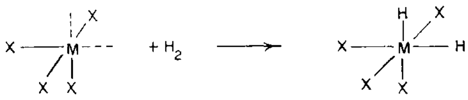
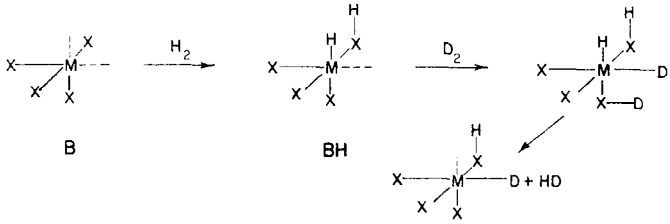


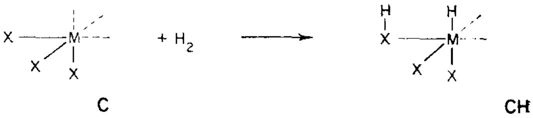
(6)



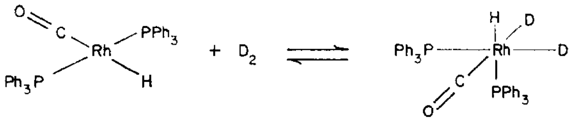
(7)

This mechanism of exchange is virtually the same as that suggested previously by others for catalysis by oxide surfaces (*1, 2, 7, 9, 17*). And we are inclined to believe that it represents one kind of mechanism which does occur.

An alternative mechanism can take place on sites of type **C**. Suppose one molecule of hydrogen combines heterolytically to form **CH**:



(8)


(9)

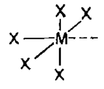
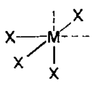
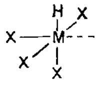
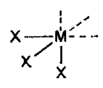
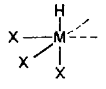
Structurally, **CH** is analogous to RhH(CO)$(PPh_3)_2$, which catalyzes the H_2–D_2 equilibration via the formation of the addition complex as in Eq. (9). Such a site (**CH**) would be expected to catalyze reactions (1)–(4) as well.

From our knowledge of the mechanism of catalysis by **I**, we can assert that if type **C** sites are not converted to type **CH** by the heterolysis of hydrogen, the H_2–D_2 equilibration will not take place, however, the addition of hydrogen to alkene should be fast; if a mixture of H_2 and D_2 is used, the addition product should be either C_nH_{2n+2} or $C_nH_{2n}D_2$ as observed. If the addition of hydrogen is faster at type **C** than type **CH** sites, and if both types are present, then the products of exchange which are formed at type **CH** sites are more likely to become saturated at type **C** than at type **CH** sites.

Exchange reaction (3), might occur at type **C** sites but this reaction would not be observed if the competing addition reaction (2), is much faster. Interestingly, Ozaki, Ai and Kimura (*21*) suggested that the isotopic mixing between C_2H_4 and C_2D_4 "seems to proceed by the reaction of π adsorbed ethylene with the hydrogen atom on the exposed metal (*17*, *21*)." The above relationships between the site structure and the reactions each affects is summarized in Table 1.

In the example presented above, we have proposed that coordinatively unsaturated cobalt atoms on the surface of cobalt oxide combine with hydrogen, either heterolytically to place a hydrido ligand on cobalt and a proton on an adjacent oxide ion, or by oxidative addition to a single cobalt atom. The first process is the slower and apparently accounts for the major part of the hydrogen which is adsorbed upon activated Co_3O_4 (*17*). Gas phase deuterium does not appear to exchange at 25°C with the adsorbed hydrogen so that the rate of desorption of the latter must be slow. Because a mixture of

TABLE 1
THE RELATION BETWEEN SITE STRUCTURE AND THE RESPONSE TO THE SUGGESTED CHARACTERIZING REACTIONS[a]

Characterizing reaction	Designation and representation				
	A	**B**	**BH**	**C**	**CH**
					
Absorption of CO or C_2H_4	+	+	+	+	+
Absorption of H_2[b]	−	+	−	+	+
H_2–D_2 equilibration	−	−	−	−	+
Alkene hydrogenation	−	−	−	+	+
C_2H_4–D_2 exchange	−	−	−	+[c]	+
C_2H_4–C_2D_4 exchange or alkene isomerization	−	−	+	−	+

[a] The characterizing reactions are ones which may take place at relatively low temperatures as on cobalt oxide (*17*).

[b] Must be distinguished from heterolytic dissociation.

[c] For ethylene, hydrogenation is liable to be faster than exchange at such sites.

H_2–D_2 undergoes rapid exchange on this catalyst, even at −78°C, a small fraction of the coordinatively unsaturated surface must adsorb H_2 or D_2 rapidly and reversibly and enable the exchange to take place (*17*). This is the role we assign to type **CH** sites which must constitute a small fraction of the number of coordinatively unsaturated cobalt atoms on the surface. Once formed, the hydrido surface complex can persist and catalyze reactions in the manner of its analog **4**.

Although the reversal of the heterolytic surface reactions could lead to exchange between hydrogen and deuterium and indeed the observed reactions involving deuterium and alkenes have been explained in this way, such mechanisms, we believe, cannot account for the very rapid exchange and hydrogenation reactions which occur at low temperatures.

Some Properties of Chromia Which May Be "Explained" by the Model

The same general concepts appear to apply to the interaction of hydrogen or deuterium with hydrocarbons on chromium oxide. Burwell *et al.* (*2*) have long recognized that homogeneous catalysis could offer analogies useful in devising mechanisms for catalysis by surfaces. In a recent detailed critical analysis of the "Chemisorptive and Catalytic Behavior of Chromia," Burwell *et al.* (*9*) discussed the creation of coordinative unsaturation to obtain catalytically active surfaces. Although aware of the possibility that both hydrogen and alkene might be bound coordinatively to the same chromium atom, they emphasized the role of heterolytic reactions. Many of their observations can be accounted for in this way, however there were several curious results which were not satisfactorily explained, for example the marked difference in the relative rate of isomerization of 1-hexene to the addition of hydrogen observed on microcrystalline chromium oxide which was activated in hydrogen compared with the result obtained on material which had been activated at the same temperature (400°C) but in helium. The activation in hydrogen gave the higher proportion of isomerization as is to be expected of a hydrido chromium site which is analogous to **4**. The reverse relationship between isomerization and hydrogenation is to be expected at the precursor site which is analogous to **2**. Alkene isomerization could also occur on **BH** sites as proposed by Tanaka, Nihira, and Ozaki (*17*).

The **CH** site should permit the rapid exchange of deuterium with benzene via the oxidative addition of benzene which would place a phenyl and two hydrido ligands at the same metallic center. The resulting structure is analogous to that recently postulated by Klabunde and Parshall (*23*) as the intermediate in the deuterium–benzene exchange reaction catalyzed by polyhydride transition metal complexes.

In the paper by Selwood (*22*) on the "Sites Active for Catalytic Hydrogen–Deuterium Equilibration over α-Chromia", we find support for the proposal that the tri-coordinatively unsaturated chromium ions (**C**), which exist on the primitive catalytic surface, are transformed by the heterolytic chemisorption of hydrogen to a hydrido species (**CH**) which then catalyzes the hydrogen–deuterium equilibration via the oxidative addition (*11*) of hydrogen (deuterium) to the same center. Selwood reported experiments with a sample of ruby which had been heated in oxygen at 500°C and quenched in helium to 25°C, a procedure shown to activate the surface. When heated slowly with a mixture of hydrogen and deuterium, the activity for exchange was observable at about 225°C and increased rapidly as the temperature was raised. If the maximum temperature attained was not over 250°C, then lowering the temperature decreased the rate of exchange, however, the activity was greater at each temperature than in the rising temperature regimen. This effect is exactly that to be expected for the mechanism of exchange we propose. The onset of exchange results from the creation of a hydrido structure (**CH**) via the heterolytic splitting of hydrogen. Once such structures are formed, the exchange may proceed more rapidly and at lower temperature, via the homolytic pathway. Although not reported as yet, similar experiments with cobalt oxide will surely show the same effect, i.e., "stabilized" cobalt oxide should catalyze the H_2–D_2 equilibration at a lower temperature than unstabilized catalyst (*17*).

Some Limitations to the Proposal and Other Mechanisms

In this account we have tried to show how a group of test reactions may be used to characterize the structures of the active centers present on the surfaces of transition metal oxides which catalyze the hydrogenation of alkenes. We have assumed that these reactions may occur at relatively low temperatures and that the mechanisms are analogous to those of the representative homogeneous catalysts **1** and **3**. Presumably other mechanisms can operate at higher temperatures so that the experimental application of the technique may be limited to the more active catalysts (*3*).

We have not discussed the evidence regarding the oxidation state of the transition element at the reactive sites on activated chromia or cobalt oxide catalysts (*9, 24*). The lower oxidation states, however, should facilitate the elementary reactions in Table 1 (*9, 13*).

Complexes other than **1** and **3** could serve as the representative homogeneous catalysts, for example $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ in place of **3** (*25*). Ando *et al.* (*26*) have discussed the mechanism of the isotopic exchange between C_2D_4 and C_2H_4 which is catalyzed by bis(triphenylphosphine)nickel(II) halides and postulate that a nickel hydride complex, formed by the heterolytic splitting of hydrogen, is the catalyst for the exchange. The H_2–D_2 equilibration is slow presumably because the reversal of the heterolytic cleavage of hydrogen is negligible and a trihydro complex is not formed (*13*). Complexes which catalyze the isomerization of alkenes and the mechanism of these reactions have been discussed by Cramer (*12*).

The reactions of hydrogen or deuterium and alkenes which occur over properly activated zinc oxide apparently belong to a different mechanistic category. Dent and Kokes (*7*) assume that the heterolysis of hydrogen on zinc oxide is an important step in the mechanism of hydrogenation and deuterium exchange reactions. Their mechanism is analogous to one postulated by Halpern, Harrod and James (*27*) for the hydrogenation of maleic acid catalyzed by ruthenium(III) chloride in aqueous hydrochloric acid. Undoubtedly some catalysts will be found to operate through the generation of free radical intermediates in analogy to the mechanisms proposed for the splitting of hydrogen by the pentacyanocobaltate(II) ion (*28*).

Our proposal is only a partial explanation of the catalytic properties of cobalt oxide and chromia. We believe, however, it is a step in the proper direction for obtaining a complete mechanism for the reactions of hydrogen and alkenes which are catalyzed by the surfaces of these oxides.

Acknowledgments

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