Catalytic Specificity

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SCOPE

Catalytic specificity refers to the particular ability of a substance or closely related group of substances to catalyze a given type of chemical transformation. Identifying the type of catalyst which is good for a particular reaction is a matter of great practical importance. In the area of heterogeneous catalysis, to which this review is limited, there are few, if any, examples where the factors determining catalytic specificity are understood in detail. However, much progress has been made in establishing patterns of variation in catalytic behavior from one substance to another for various types of reactions. In particular, broad relationships are often evident between the catalytic activity of an element or its compounds and the position of the element in the periodic table. These relationships introduce a measure of order into heterogeneous catalysis and will be useful in the development of a more fundamental understanding of the subject.

The present review considers a variety of classes of reactions from the standpoint of assessing patterns of variation in behavior among catalysts. The types of reactions considered include hydrogenation, hydrogenolysis, isomerization, ammonia synthesis and decomposition, oxidation, and the decomposition of alcohols and organic acids. Relationships between catalytic activities and the chemisorption properties of reactants are discussed repeatedly. Both metal and oxide type catalysts are considered. However, most of the emphasis is on metals, for which more extensive data comparing specific catalytic activities are available.

CONCLUSIONS AND SIGNIFICANCE

Much has been learned about the specificity of catalytic action from systematic studies of a reaction over a series of catalysts. In some cases the degree of specificity is so high that only one catalyst is known for a reaction, as in the case of the oxidation of ethylene to ethylene oxide on silver. In the more usual case, however, a given reaction will occur on a number of related catalysts, and it is instructive to determine the pattern of variation of activity from one catalyst to another. This seems to have been accomplished most satisfactorily for metal catalysts, where characteristic patterns have been established for reactions such as the hydrogenation, hydrogenolysis, and oxidation of hydrocarbons, and the decomposition of ammonia. For a given series of metal catalysts, the pattern of activity variation depends on the nature of the reaction. For example, ethane hydrogenolysis gives a pattern very different from that found with cyclohexane dehydrogenation, as demonstrated strikingly on copper-nickel alloys.

In considering patterns of activity variation among catalysts, one can generally rationalize the results in terms of a rather broad principle relating catalytic activity to the adsorption properties of the reactants. According to this principle, maximum activity results when chemisorption of the reactant is fast but not very strong. If the adsorption bond is too strong, the catalyst will tend to be fully covered by a surface species which is too stable to undergo reaction. This represents one extreme. At the other extreme, if chemisorption of the reactant is slow, the reaction may be severely limited by the adsorption step. Optimum catalytic activity corresponds to an intermediate degree of coverage of the surface by the adsorption complex undergoing reaction.

Perhaps the most fascinating aspect of catalysis is specificity. In heterogeneous catalytic processes occurring on solid surfaces, it has long been known that the chemical nature of the surface is important; that is, the role of the surface is more than simply concentrating reactants in an adsorbed layer. An example which has often been used to illustrate this point is the reaction of ethanol over chemically different types of surfaces (see, for example, Thomson and Webb, 1968). Over copper catalysts the observed reaction is dehydrogenation to acetaldehyde, while on alumina the reaction is dehydration to ethylene. Similarly, formic acid undergoes predominantly dehydrogenation to carbon dioxide and hydrogen over a variety of metal catalysts (Fahrenfort et al., 1960), but on certain oxide catalysts the major reaction is dehydration to yield carbon monoxide and water (Mars, 1960).

The area of hydrocarbon oxidation provides some striking illustrations of catalytic specificity. For example, the only known catalysts for the selective partial oxidation of ethylene to ethylene oxide contain silver as the active component (see, for example, Griffith and Marsh, 1957). Interestingly, the same silver catalysts are not effective for the oxidation of propylene to propylene oxide. When propylene undergoes partial oxidation, the predominant product is acrolein. This reaction occurs efficiently on a limited number of catalysts, including cuprous oxide and bismuth-molybdenum oxide systems (Voge and Adams, 1967). In the case of Group VIII metals such as platinum, palladium, and rhodium, the catalytic activity is high for oxidation of a variety of olefins, including ethylene and propylene, but the reaction is predominantly one of complete oxidation to carbon dioxide and water (Patterson and Kemball, 1963).

The catalytic synthesis of ammonia from elemental nitrogen and hydrogen is a highly important industrial reaction in which the specificity of catalytic action is again very evident. The reaction is catalyzed satisfactorily by only a few metals. Of these, iron is the metal of most interest, as evidenced by its extensive commercial application in ammonia synthesis. Among the Group VIII metals, which are generally good catalysts for reactions involving hydrogen, the only active metals other than iron are ruthenium and osmium.

Another area of catalysis with interesting specificity aspects is that comprising the reactions of hydrocarbons in the presence of hydrogen. In this area the Group VIII metals occupy a key position in the catalysis of hydrogenation, dehydrogenation, and hydrogenolysis reactions of hydrocarbons. Of particular interest, comparisons of the catalytic activities of these metals reveal characteristic patterns which depend strongly on the type of reaction. Hydrogenation and dehydrogenation reactions give activity patterns strikingly different from those observed for hydrogenolysis reactions (Sinfelt, 1973a). This behavior is observed dramatically with certain bimetallic catalysts when the metallic composition is varied (Sinfelt et al., 1972). Another intriguing example of specificity is found in the isomerization of alkanes on metals. The reaction is limited to only a few metals, of which platinum is the most prominent example (Anderson and Baker, 1963).

As the foregoing paragraphs suggest, specificity is a characteristic and highly important feature of catalysis. The present review treats the question of catalytic specificity by a consideration of selected examples from the area of heterogeneous catalysis. Particular attention is given to examples for which sufficient data are available to establish clear patterns of variation of activity from one catalyst to another.

HYDROGENATION

Hydrogenation is an area of great practical importance in catalysis and one which has received considerable attention with regard to the mechanism of catalytic action. The area is a very broad one, encompassing the reactions of hydrogen with a number of different types of molecules. The discussion here is limited to the hydrogenation of unsaturated hydrocarbons. For such reactions, the active catalysts are the transition metals, especially the Group VIII metals.

The hydrogenation of ethylene has been employed very extensively as a model reaction in fundamental studies of metal catalysis. The catalytic activities of a number of metals have been compared for this reaction. The variation in activity is associated with differences in the pre-exponential factor of the rate constant rather than differences in activation energy. Of the various Group VIII metals which are active for the reaction, rhodium exhibits the maximum activity. There is an inverse correlation of activities with the heats of adsorption of ethylene and hydrogen on the metals. The pattern of variation of catalytic activity among the metals has been rationalized in terms of a geometrical factor relating activity to the lattice spacing of the metal (Beeck, 1945), or an electronic factor relating activity to the percentage *d*-character of the metallic bond (Boudart, 1950). These points have been discussed in some detail in a review by Boudart (1961).

The activities of a number of metals supported on silica have been compared for ethylene hydrogenation by Schuit and van Reijen (1958). Their results are summarized in Figure 1, which relates the activity of the metal to its position in the periodic table. The figure is divided into three fields separating the metals of the first, second, and third transition series. In general, the Group IB metals (Cu, Ag, Au), which are immediately after the Group VIII metals in the periodic table, are much less active than the latter for hydrogenation, as indicated by the data on copper in the figure. Also, the metals just preceding the Group VIII metals in the periodic table are less active than the latter, as is well known. Thus, the Group VIII metals are the most active hydrogenation catalysts. Within Group VIII, the activity pattern in the second triad of metals (Ru, Rh, Pd) is different from that in the first triad (Fe, Co, Ni) and third triad (Os, Ir, Pt). In the second triad the Group $VIII_2$ metal (rhodium) has the highest activity. However, in the first and third triads, the Group $VIII_3$ metal (nickel or platinum) is the most active. Similar findings regarding activity patterns have been made in the hydrogenation of cyclopropane to propane on the Group VIII metals (Dalla Betta et al., 1970). Although cyclopropane is formally a saturated hydrocarbon, it is well known that its chemical behavior is similar to that of an olefin.

A comparison of the catalytic activities of the metals iron, cobalt, nickel, and copper for the hydrogenation of the triple bond in acetylene reveals a pattern of variation of activity similar to that shown for these metals in the hydrogenation of ethylene (Bond, 1962). Catalytic activity patterns in the hydrogenation of benzene on the Group VIII metals are roughly similar to those found for ethylene hydrogenation. Comparisons of activities of the metals within the first and second triads of Group VIII are given in Figure 2, based on the data of Schuit and Van Reijen (1958). An activity pattern is not shown for the metals of the third triad, since platinum was the only one of these metals investigated. Interestingly, platinum was found to be the most active metal for benzene hydrogenation, exhibiting an activity slightly more than twice the activity found for rhodium. However, it should be noted that the variation of activity among the metals platinum, palladium, rhodium, and ruthenium is small in any case, amounting to a factor of only four. These metals are all more active than the metals of the first triad by one to two orders of magnitude.

In the several examples of hydrogenation reactions of unsaturated hydrocarbons considered here, it is clear that the Group VIII metals are the catalysts of interest. When

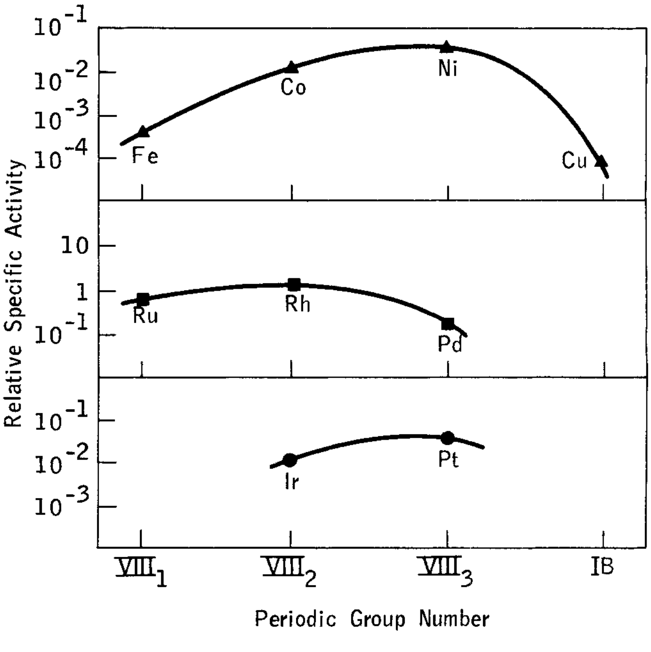

Fig. 1. Catalytic activities of silica supported metals for ethylene hydrogenation. The three fields in the figure separate the metals of the first, second, and third transition series of the Periodic Table (Schuit and van Reijen, 1958).

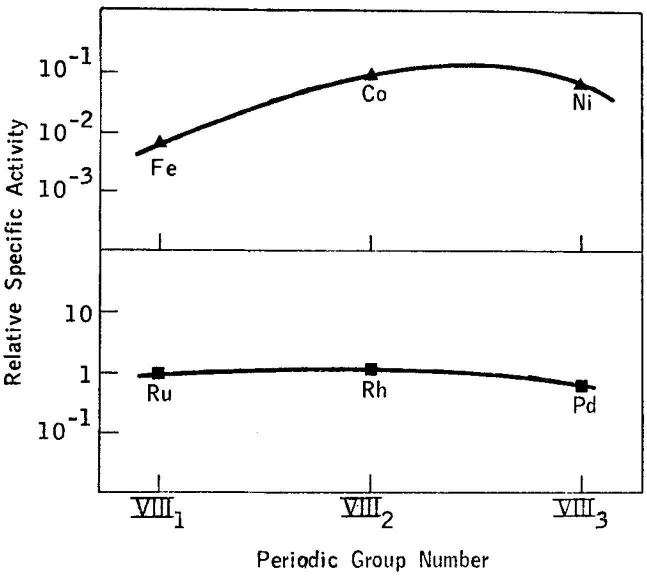

Fig. 2. Catalytic activities of silica supported metals for benzene hydrogenation at 100°C. The two fields in the figure separate the metals of the first and second transition series of the Periodic Table (Schuit and van Reijen, 1958).

metals immediately before or after Group VIII metals are compared with the latter, the maximum catalytic activity is found within Group VIII. In a general way, this may be rationalized in terms of the strength of adsorption of the reactants. On metals such as tantalum, chromium, molybdenum, or tungsten, in Group VA and Group VIA, the adsorption bonds between the reactants and surface are too strong. The adsorbed species are then too stable for catalysis to proceed readily. In the case of Group IB metals, the problem is just the opposite, in that hydrogen is not even chemisorbed on these metals. The intermediate strengths of adsorption attained with the Group VIII metals correspond to high catalytic activity. While the Group VIII metals as a whole can be differentiated from metals of other groups with regard to heats of adsorption, it is more difficult to assess the influence of this factor in considering the activity differences among the metals within Group VIII itself. Where information is available, the differences among the metals are small, and it is questionable how much significance can be attached to them.

HYDROGENOLYSIS

Hydrogenolysis reactions of hydrocarbons involve the rupture of carbon-carbon bonds and the formation of carbon-hydrogen bonds. The reactions are catalyzed by various transition metals. The simplest example is the reaction of ethane with hydrogen to yield methane, the kinetics of which were investigated originally on nickel (Morikawa et al., 1936), and subsequently on cobalt (Taylor and Taylor, 1939) and iron (Cimino et al., 1954). More recently, studies of the kinetics of ethane hydrogenolysis have been extended to platinum (Sinfelt, 1964b; Sinfelt et al., 1965), other Group VIII noble metals (Sinfelt and Yates, 1967; 1968), and rhenium (Yates and Sinfelt, 1969). A comparison of metals as hydrogenolysis catalysts reveals a striking variation in activity, even among such similar metals as the noble metals of Group VIII. Specific catalytic activities of all of the metals of Group VIII and of rhenium in Group VIIA for the hydrogenolysis of ethane to methane are given in Figure 3 (Sinfelt, 1973a). The figure has three separate fields representing the metals of the first, second, and third transition series. The metals were supported on silica, and surface areas were determined by hydrogen chemisorption. The specific activities are relative reaction rates per unit surface area of metal at a temperature of 205°C and ethane and hydrogen partial pressures of 0.030 and 0.20 atm., respectively. Activities of the Group IB metals (copper, silver, and gold) are not shown in the figure, but they are much lower than the activities of the least active Group VIII metals (Sinfelt, 1973a).

In comparing the catalytic activities of metals for ethane hydrogenolysis, let us consider the variation in activity as a function of the position of the metal within a given period of the periodic table. The most complete data are available for the metals of the third transition series. Beginning with rhenium in Group VIIA, and proceeding in the direction of increasing atomic number to osmium, iridium, and platinum in Group VIII and on to gold in Group IB, the hydrogenolysis activity attains a maximum value at osmium. From osmium to platinum alone, the activity decreases by seven orders of magnitude. A similar variation is observed from ruthenium to palladium in the second transition series. It is probable that the hydrogenolysis activity in the second transition series attains a maximum value at ruthenium, as it does at osmium in the third transition series. This is supported by recent data on the Group VIA metal, molybdenum, in the second transition series. The data indicate that the hydrogenolysis activity of this metal is virtually negligible compared to that of ruthenium (Sinfelt and Yates, 1971). The hydrogenolysis of ethane on molybdenum proceeds readily only at temperatures high enough to cause carbiding of the

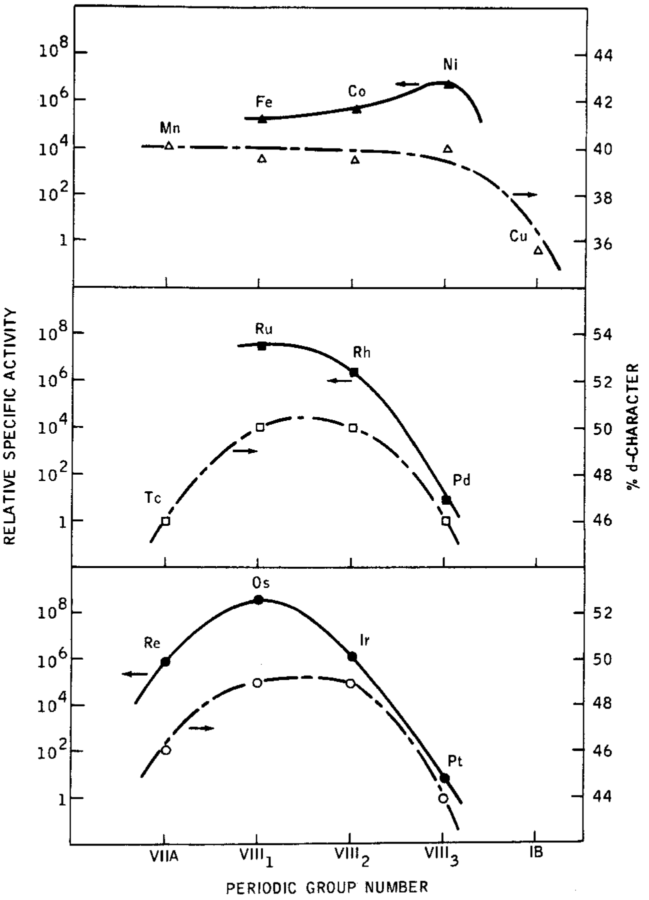

Fig. 3. Catalytic activities of metals for ethane hydrogenolysis in relation to the percentage *d*-character of the metallic bond. The closed points represent activities compared at a temperature of 205°C and ethane and hydrogen pressures of 0.030 and 0.20 atm., respectively, and the open points represent percentage *d*-character. Three separate fields are shown in the figure to distinguish the metals in the different long periods of the Periodic Table (Sinfelt, 1973a).

molybdenum, that is, about 375 to 400°C.

In the first transition series, the Group VIII metals (iron, cobalt, and nickel) are much more active for hydrogenolysis than copper in Group IB. In this respect, the first transition series is very similar to the second and third transition series just discussed. However, maximum catalytic activity in the first transition series is observed for the metal in the third subgroup within Group VIII, that is, nickel, whereas in the second and third transition series the maximum activity is observed for the metal in the first subgroup within Group VIII, namely, ruthenium or osmium. Thus, the pattern of variation of hydrogenolysis activity among the non-noble Group VIII metals of the first transition series is somewhat different from that observed for the noble Group VIII metals of the second and third transition series. This tends to parallel known chemical differences between elements of the first transition series on the one hand and the corresponding elements of the second and third transition series on the other (see, for example, Cotton and Wilkinson, 1962).

Included with the plots of hydrogenolysis activities of the metals in Figure 3 are plots of the percentage *d*-character of the metallic bond, a quantity introduced in the valence bond theory of metals to represent the extent of participation of *d*-orbitals in the bonding between atoms in a metal lattice (Pauling, 1949). For the metals within a given transition series, the patterns of variation of hydrogenolysis activity and percentage *d*-character from one metal to another are similar. Further consideration of the relation between hydrogenolysis activity and percentage *d*-character distinguishes again the metals of the first transition series (which include iron, cobalt, and nickel) from the metals of the second and third transition series (which include the Group VIII noble metals). The hydrogenolysis activities of iron, cobalt, and nickel in the first transition series are comparable to those of metals with significantly higher *d*-character in the second and third transition series. Thus, while there is a correlation between hydrogenolysis activity and percentage *d*-character, this parameter alone is not adequate for characterizing the catalytic activity of transition metals for hydrogenolysis (Sinfelt, 1969).

Activity patterns of metals for the hydrogenolysis of alkanes are not strongly affected by the particular alkane used as a reactant. However, the rate of hydrogenolysis increases with increasing carbon number of the alkane (Sinfelt, 1973a). Data of Anderson and Avery (1966) indicate that the most important difference is between ethane and other alkanes containing more than two carbon atoms. They observe that the activation energies for hydrogenolysis of *n*-butane, isobutane, isopentane, and neopentane are nearly the same, but much lower than that found for ethane. They suggest that the alkanes other than ethane form 1,3-adsorbed intermediates, while ethane forms a 1,2-adsorbed intermediate (Figure 4). In the case of neopentane, a 1,2-adsorbed species is not even possible. Presumably, a 1,3-adsorbed intermediate has a higher reactivity for carbon-carbon scission than does a 1,2-adsorbed intermediate. However, the increase in rate of hydrogenolysis with increasing carbon number could in part be attributable to lower average dissociation energies of carbon-carbon bonds in larger alkane molecules (Semenov, 1958).

In the hydrogenolysis of saturated hydrocarbons possessing a number of carbon-carbon bonds, which are not all identical, there may be different rates of rupture of carbon-carbon bonds at different locations in the molecule. It is particularly interesting that the distribution of primary hydrogenolysis products (that is, the cracking pattern) depends on the metal catalyst used. A classical example of catalytic specificity is the highly selective attack of nickel catalysts on the terminal carbon-carbon bonds in alkanes. For example, in the hydrogenolysis of *n*-hexane on a nickel-silica catalyst at 180°C, the only products observed at very low conversion are methane and *n*-pentane formed in equimolar amounts (Matsumoto et al., 1970). Similarly, the hydrogenolysis of 2-methylpentane and 3-methylpentane yields methane, *n*-pentane, and isopentane as the only primary products at low conversions, the mole fraction of methane in the product corresponding closely to the combined mole fraction of normal and isopentanes. The mole ratio of isopentane to *n*-pentane in the products of hydrogenolysis of 2-methylpentane and 3-methylpentane is close to 0.5 and 2.0, respectively, which is expected on the basis of purely statistical considerations of the products resulting from scission of terminal carbon-carbon bonds. However, platinum catalysts contrast markedly with nickel catalysts, in that the rupture of different carbon-carbon bonds is nonselective. In the hydrogenolysis of *n*-hexane over a platinum-silica catalyst, the rates of rupture of various carbon-carbon bonds are nearly the same, giving a spectrum of primary products comprising all of the normal alkanes from methane through *n*-pentane in comparable molar quantities.

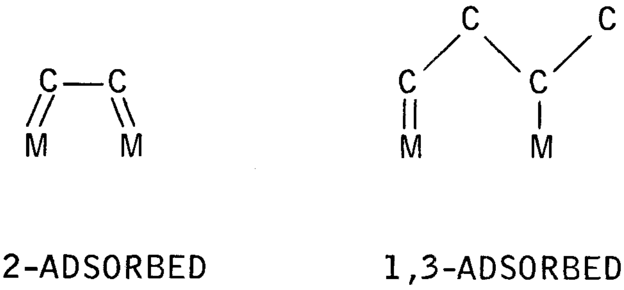

Fig. 4. Examples of 1,2-adsorbed and 1,3-adsorbed hydrocarbon species. The symbol *M* represents a surface metal atom.

The striking specificity possible in the hydrogenolysis of hydrocarbons on metals is clearly demonstrated by recent studies conducted in our laboratory on the hydrogenolysis of *n*-heptane at low conversion levels on a number of Group VIII noble metal catalysts (Carter et al., 1971). To eliminate carrier effects of the kind operative in bifunctional metal-acidic oxide catalysts, unsupported metal powders were employed. The distribution of products from the hydrogenolysis of *n*-heptane varies markedly among the Group VIII noble metals (Table 1). On palladium and rhodium the terminal carbon-carbon bond is attacked almost exclusively, yielding methane and *n*-hexane as the products. However, on the other metals, especially platinum and iridium, the cracking is much less selective. No obvious relation exists between the level of hydrogenolysis activity and the type of cracking pattern observed. For example, platinum and palladium, with similar low hydrogenolysis activities, exhibit markedly different distributions of primary products. Furthermore, iridium and rhodium give much different product distributions, although both metals are highly active for hydrogenolysis. The highly selective rupture of the terminal carbon-carbon bond on palladium and rhodium has been observed by others, for example, in *n*-hexane hydrogenolysis on a palladium-silica catalyst (Matsumoto et al., 1971) and in *n*-butane hydrogenolysis on an evaporated rhodium film (Anderson and Baker, 1963). The less selective type of cracking pattern on platinum has been observed often. In recent discussions of the mechanism of hydrogenolysis and isomerization of saturated hydrocarbons on platinum, it has been suggested that charge transfer from the adsorbate to the metal occurs (Anderson and

Table 1. Distribution of *n*-Heptane Hydrogenolysis Products over Metals[a]

Metal	Temp., °C	% Total conversion	Distribution of hydrogenolysis products, Mole %[b]					
			C_1	C_2	C_3	nC_4	nC_5	nC_6
Pd	300	6.4	46	4	—	—	4	46
Rh	113	2.9	42	5	4	3	5	41
Ru	88	4.0	28	12	13	12	10	25
Pt	275	2.3	31	13	17	16	9	14
Ir	125	1.5	21	21	15	14	14	15

[a] Conditions: 1 atm, H_2/nC_7 mole ratio = 5.
[b] All products are *n*-paraffins.

Avery, 1967; Matsumoto et al., 1970), with the result that a carbonium ion-like intermediate is formed. The extensive cracking of internal carbon-carbon bonds in alkanes, and the simultaneous skeletal isomerization reaction, are consistent with such a suggestion. Reactions of this type are observed on acid catalysts and are generally associated with carbonium ion mechanisms.

In the hydrogenolysis of the higher alkanes on the non-noble Group VIII metals (that is, iron, cobalt, and nickel), the mode of cracking is different from that observed on the noble metals of Group VIII (Matsumoto et al., 1970, 1971). In general, the products of hydrogenolysis are consistent with a reaction scheme involving successive demethylation of the hydrocarbon chain. According to this scheme, cracking occurs only at terminal carbon-carbon bonds so that one of the fragments is always a C_1 species which is hydrogenated to form methane. The other fragment then has one of two fates. It can undergo further cracking at the terminal carbon-carbon bond to produce additional methane, or it can be hydrogenated and desorbed into the gas phase. On moving from nickel to cobalt to iron, one finds that the initial distribution of products shifts markedly in the direction of lower carbon number alkanes, suggesting that desorption of products becomes strongly limiting.

The successive demethylation scheme of hydrogenolysis just discussed for iron, cobalt, and nickel does not apply to the noble metals of Group VIII. The amounts of methane observed on the latter are much lower than would be expected if the hydrogenolysis occurred by successive demethylation steps. Thus, we have another indication that the noble and non-noble metals of Group VIII behave as two separate classes with regard to their catalytic properties in the hydrogenolysis of hydrocarbons.

HYDROGENOLYSIS AND DEHYDROGENATION ON BIMETALLIC CATALYSTS

Metal alloys have been employed by a number of workers to investigate the electronic factor in catalysis (Baker and Jenkins, 1955). Alloys consisting of a Group VIII metal and a Group IB metal, such as copper-nickel, have been investigated extensively for such reactions as the hydrogenation of benzene (Hall and Emmett, 1958; van der Plank and Sachtler, 1968) and ethylene (Hall and Emmett, 1959; Campbell and Emmett, 1967). It is reasonable to expect the dehydrogenation of cyclohexane to benzene to exhibit behavior similar to benzene hydrogenation when copper is added to nickel. However, it does not follow that conclusions based on studies of these reactions would be applicable to ethane hydrogenolysis. Indeed, recent data on ethane hydrogenolysis indicate a very different effect of adding copper to nickel.

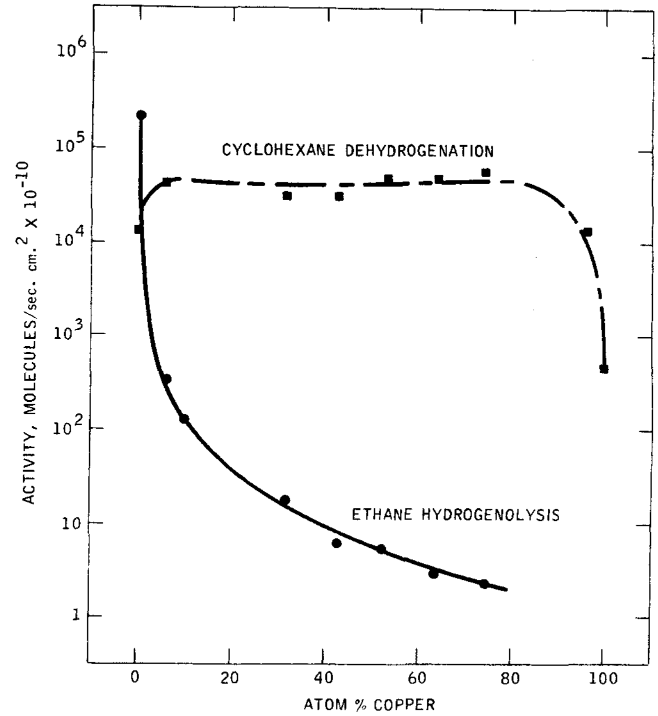

Fig. 5. Activities of copper-nickel alloy catalysts for the hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene. The activities refer to reaction rates at 316°C. Ethane hydrogenolysis activities were obtained at ethane and hydrogen pressures of 0.030 and 0.20 atm., respectively. Cyclohexane dehydrogenation activities were obtained at cyclohexane and hydrogen pressures of 0.17 and 0.83 atm., respectively (Sinfelt, Carter, and Yates, 1972).

Specific activities of a series of copper-nickel alloy catalysts for ethane hydrogenolysis to methane and cyclohexane dehydrogenation to benzene are shown in Figure 5 as a function of the catalyst composition (Sinfelt et al., 1972). The catalysts were finely divided metal granules with surface areas of 1-2m^2/g. The specific activities in Figure 5 are reaction rates at 316°C. The catalytic activity of nickel for ethane hydrogenolysis decreases markedly and continuously as copper is alloyed with it. Addition of only 5 atom % copper decreases the hydrogenolysis activity by three orders of magnitude. With further addition of copper, the activity continues to decline such that the activity of a catalyst containing about 60 atom % copper is five orders of magnitude lower than that of pure nickel. In marked contrast to the ethane hydrogenolysis results, the catalytic activity of nickel for cyclohexane dehydrogenation increases initially with addition of small amounts of copper. The activity is then nearly constant as alloy composition is varied over a wide range but finally decreases sharply as the composition approaches pure copper. Interestingly, the activity of a catalyst containing about 95 atom % copper is equivalent to that of the pure nickel catalyst, although the activity of the copper itself is about two orders of magnitude lower than that of the nickel. The initial promotional effect of copper on nickel has also been reported for the hydrogenation of benzene and ethylene (Hall and Emmett, 1958; 1959).

In considering the effect of copper on the activity of nickel for ethane hydrogenolysis, we recall the correlation of hydrogenolysis activity with the percentage *d*-character of the metallic bond for metals within a particular transition series (Figure 3). According to this correlation, the hydrogenolysis activity of nickel should decrease when copper is alloyed with it, since the percentage *d*-character decreases. However, the activity decreases much more sharply than percentage *d*-character with the initial incremental additions of copper to nickel. This could be reconciled if there was a surface region in the alloys with a copper content much higher than that of the bulk. The percentage *d*-character corresponding to the surface composition would then be lower than one would expect on the basis of the bulk composition. Evidence for a marked difference between the surface and bulk compositions of dilute copper-nickel alloys has been obtained from hydrogen chemisorption studies (van der Plank and Sachtler, 1967; Cadenhead and Wagner, 1968; Sinfelt et al., 1972). The method is based on the observation that strong chemisorption of hydrogen does not occur on copper. The data show that the amount of strongly chemisorbed hydrogen decreases severalfold when only a few percent of copper is added to nickel. This is consistent with a marked concentration of copper in the surface.

The very different effects of copper on the catalytic activity of nickel for ethane hydrogenolysis and cyclohexane dehydrogenation may be due to differences in the nature of the rate determining steps involved. In proceeding with a discussion along these lines, it will be assumed that the strength of adsorption of hydrocarbons on nickel decreases when copper is alloyed with the nickel, by analogy with hydrogen chemisorption data. If the surface coverage by the reaction product is very high, such that desorption controls the reaction rate, a decrease in the heat of adsorption would increase the rate. This may be the case in cyclohexane dehydrogenation, that is, desorption of the benzene product controls the reaction rate. On addition of copper to nickel, the heat of adsorption of benzene would be expected to decrease, leading to a corresponding decrease in the activation energy of the desorption step. This suggestion is based on earlier work on the dehydrogenation of methylcyclohexane to toluene on platinum (Sinfelt et al., 1960b) where it was concluded that the reaction rate was limited by desorption of the toluene product. This would account for the initial enhancement of the rate of cyclohexane dehydrogenation with addition of the first increments of copper to nickel. The range of composition (6 to 74% copper) over which the rate is essentially constant is probably characterized by a relatively small variation of the heat of adsorption of the hydrocarbon. At very high copper content (>95 atom %) the reaction rate is probably limited by a step prior to the final product desorption step. The reaction rate could then be adversely affected by a decrease in the heat of adsorption of a hydrocarbon intermediate formed prior to benzene on the surface, thus leading to a decrease in rate as the catalyst composition approaches pure copper. In the case of ethane hydrogenolysis, the reaction intermediate is probably a highly unsaturated, dicarbon surface residue with both carbon atoms bonded to metal surface atoms (Sinfelt, 1969). It seems reasonable that the strength of bonding between the two carbon atoms in such a surface intermediate would vary in an inverse manner with the strength of bonding of the carbon atoms to the surface. Consequently, the rupture of the carbon-carbon bond would be facilitated by an increase in the heat of adsorption, and inhibited by a decrease. If such carbon-carbon bond rupture is the rate limiting step in the reaction, the rate of reaction should decrease as the heat of adsorption decreases, corresponding to addition of copper to nickel. This would appear to be the case over the whole range of composition in the copper-nickel catalyst system.

The different behavior of copper-nickel alloys for the ethane hydrogenolysis and cyclohexane dehydrogenation reactions has also been observed for bimetallic catalysts containing copper and a Group VIII metal other than nickel, for example, ruthenium and osmium (Sinfelt, 1973b). In general, the addition of a Group IB metal to a Group VIII metal has been found to inhibit markedly the hydrogenolysis activity of the latter while having a much smaller effect on dehydrogenation activity (Sinfelt et al., 1971). This has been found even for bimetallic catalysts in which the component metals exhibit very low miscibility in the bulk, as is the case for the ruthenium-copper and osmium-copper systems just mentioned. Furthermore, the behavior has been observed for such bimetallic systems in a state of very high dispersion on a carrier where the total metal concentration is of the order of only 1 to 2%. Despite the low metal concentration and attendant low coverage of the carrier surface by the metals, there must be intimate interaction between the metal components. If the individual metals existed as separate entities on the carrier, one would expect to find a simple type of additive catalytic behavior of the individual metallic entities. In view of the strong interaction between the metallic components as indicated by the catalytic data, it has been concluded that highly dispersed bimetallic clusters exist on the carrier surface (Sinfelt, 1973b). The existence of such bimetallic clusters in systems with severe miscibility limitations in the bulk implies a strong effect of the degree of metal dispersion on the stability of the bimetallic phase. Consequently, a bimetallic phase of this type would exist only for sufficiently small metal crystallites, so that conditions favoring extensive metal crystal growth would give phase separation. Experimental evidence in support of such a phenomenon has been reviewed recently by Ollis (1971). There appears to be no reason why the phenomenon should be limited to bimetallic systems. The possibility of forming highly dispersed polymetallic clusters introduces much flexibility in the design of supported metal catalysts.

A recent investigation by Ponec and Sachtler (1972) on nickel and nickel-copper alloy films is of interest in relation to the catalytic behavior of the bimetallic systems discussed in the previous paragraphs. These workers were concerned primarily with the exchange reaction of cyclopentane with deuterium to yield deuterocyclopentanes. However, hydrogenolysis of the cyclopentane also occurred as a side reaction. The effect of adding copper to nickel was much greater for the hydrogenolysis reaction than for the multiple exchange reaction. The data thus suggest that a reaction involving the rupture of carbon-hydrogen bonds is much less sensitive to alloying than is a reaction involving rupture of carbon-carbon bonds. In this respect the results are very similar to the findings contrasting the behavior of dehydrogenation and hydrogenolysis reactions as copper is incorporated with various Group VIII metals in bimetallic catalysts

The great decrease in the hydrogenolysis activity observed with these bimetallic catalysts may be considered from two points of view. First, since it has been concluded previously that the intermediates in hydrogenolysis reactions are highly unsaturated hydrocarbon residues multiply bonded to surface metal atoms (Sinfelt, 1969), one might expect the reactions to be sensitive to surface structure and composition. If atoms of the active Group VIII metal in the surface are interspersed extensively with copper atoms, the concentration of adsorbed intermediate could be very sensitive to restrictions in the number of sites comprising multiplets of atoms of the active metal. This may be considered as the role of a geometric factor in the catalysis. Second, the presence of the copper may affect the properties of the Group VIII metal atoms in the surface so that the strength of bonding of these atoms with hydrocarbons is modified. This may be viewed as the electronic factor. In view of the very large effects of copper on the hydrogenolysis activities of various Group VIII metals, it seems probable that an electronic factor is involved in addition to a purely geometric factor. By contrast, reactions of hydrocarbons involving rupture of only C-H bonds, such as cyclohexane dehydrogenation or cyclopentane-deuterium exchange, would appear to be relatively insensitive to these same geometric and electronic factors. Employing the terminology of Boudart et al. (1968), one might designate the hydrogenolysis reactions *demanding* and the cyclohexane dehydrogenation and cyclopentane-deuterium exchange reactions *facile*.

ISOMERIZATION OF ALKANES

The isomerization of alkanes is a reaction of great importance in petroleum chemistry. Historically the reaction has been associated with acid catalysts such as aluminum chloride and aluminum bromide (Pines, 1948; Condon, 1958), or with bifunctional metal-acidic oxide catalysts such as platinum supported on alumina or silica-alumina (Sinfelt, 1964a). The former are commonly known as Friedel-Crafts type catalysts (Prettre, 1963) and are frequently promoted with hydrogen halides. They are used at temperatures in the range of 25 to 150°C. The latter are well known for their extensive application in the catalytic reforming of petroleum naphthas (Weisz and Prater, 1957; Ciapetta et al., 1958) in which isomerization is one of the contributing reactions. The temperatures employed with the bifunctional metal-acidic oxide catalysts are commonly in the range of 300 to 500°C, and elevated pressures of hydrogen (10 to 35 atm.) are used to suppress formation of carbonaceous residues on the surface of the catalyst. The residues lead to deactivation of the catalyst. It is generally accepted that isomerization of alkanes on either Friedel-Crafts or bifunctional metal-acidic oxide catalysts proceeds by a carbonium ion type of mechanism. In the case of bifunctional metal-acidic oxide catalysts, the available evidence indicates that olefins are intermediates in the reaction (Mills et al, 1953). An olefin is formed by dehydrogenation of an alkane on the metal sites of the catalyst, from which it migrates to acidic sites to undergo a skeletal rearrangement yielding an isomer of the original olefin. The isomerized olefin then returns to a metal site to be hydrogenated to the corresponding isoparaffin, thus completing the reaction. The rearrangement of the olefin intermediate on the acid sites is the step which is associated with a carbonium ion mechanism and is commonly the rate limiting step in the reaction (Sinfelt et al., 1960a; 1962). A reaction sequence involving transport of olefin intermediates from metal to acidic sites via the gas phase gives a good account of much experimental data in alkane isomerization. This mechanism of transport was originally suggested on the basis of experiments with catalyst mixtures, in which the metal and acid sites were physically separated on different particles (Weisz and Swegler, 1957; Hindin et al., 1958). Such mixtures were shown to be very effective catalysts for isomerization, while the individual components of the mixtures were not.

Although it has long been thought that an acid component is a necessary part of an alkane isomerization catalyst, research in recent years has provided several examples showing that the reaction can occur on certain metals in the absence of an acidic component. For example, Anderson and Baker (1963) observed isomerization of n-butane and isobutane on evaporated films of certain metals, especially platinum. Subsequent work by Anderson and Avery (1966) and by Boudart et al. (1968) showed that neopentane was isomerized to isopentane over various forms of platinum catalysts. The isomerization of n-hexane (Barron et al., 1966) and n-heptane (Carter et al., 1971) on monofunctional platinum catalysts has also been reported recently. These examples provide clear evidence of a metal catalyzed isomerization process which does not require the presence of a conventional acidic component in the catalyst. This does not challenge the commonly accepted mode of action of bifunctional metal-acidic oxide catalysts in isomerization, which is supported by much experimental evidence. It simply says that a purely metal catalyzed process can occur. The available data at conditions commonly employed with commercial reforming catalysts indicate that a purely metal catalyzed process does not contribute significantly to the overall isomerization reaction on a bifunctional catalyst. Nevertheless, the metal catalyzed alkane isomerization reaction is of interest for what it may reveal about hydrocarbon chemistry at metal surfaces. A mechanism for the reaction has been proposed by Anderson and Avery (1967). According to these investigators, the reaction involves a 1,3-adsorbed intermediate. The transformation then proceeds as shown in Figure 6. The 1,3-adsorbed species has one sp^2 carbon atom doubly bonded to a surface metal atom M. In the course of the reaction, the state of hybridization of this carbon atom changes, which in turn requires a shift in the valency of the surface metal atom. If there is sufficient tendency for electron transfer to occur from the sp^2 carbon atom to the metal, the properties of the adsorbed hydrocarbon species approach those of a carbonium ion, and the rearrangement of the carbon skeleton becomes energetically more favorable. The possibility of carbonium ion-like intermediates in hydrocarbon reactions on platinum has also been considered by other workers (Matsumoto et al., 1970).

Boudart and Ptak (1970) have investigated the reactions of neopentane on all the metals of Group VIII, and on copper and gold as well. The work was done to determine if there were metals other than platinum capable of isomerizing neopentane. It was found that iridium and gold also catalyzed the reaction. On these metals the activity for isomerization was roughly of the same order as the activity for hydrogenolysis. For the metals other than platinum, iridium, and gold, no isomerization could be detected. The authors suggest that two requirements must be met in a metal which is capable of isomerizing neopentane. First, the metal must be sufficiently electronegative to promote electron transfer from the adsorbed hydrocarbon to the metal. This appears to be a necessary but not sufficient condition. Platinum, iridium, and gold are significantly more electronegative than iron, cobalt, nickel, and copper. However, platinum and iridium have the same electronegativity as the other four Group VIII noble metals on the basis of Pauling's scale of electronegativities. Consequently, another distinguishing feature is needed. This is supplied by the author's second requirement,

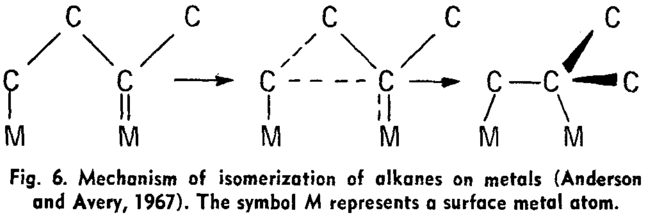

Fig. 6. Mechanism of isomerization of alkanes on metals (Anderson and Avery, 1967). The symbol M represents a surface metal atom.

namely, that the metal must have the capability of changing its surface valency for isomerization to proceed according to the Anderson and Avery mechanism. Evidence for a variable surface valency limited to the metals platinum, iridium, and gold is discussed by the authors. In the case of platinum and iridium, Plummer and Rhodin (1968) found from field desorption measurements that the binding energies and hence effective valencies of atoms of these metals on tungsten varied with the particular plane on which the platinum and iridium atoms were adsorbed. This variation was not observed with a number of other metals. In the case of gold where surface rearrangements have been observed in low energy electron diffraction studies, Palmberg and Rhodin (1968) suggest that the phenomena are due to a particular sensitivity of the effective valence of gold to the nature and number of neighboring atoms. The sensitivity is attributed to the ease of promotion of the $5d^{10}6s^1$ electronic configuration of atomic gold to an excited state with a $5d^96s^2$ electronic configuration. According to these authors, surface rearrangements of platinum can also be attributed to a similar ease of electronic promotion, in this case from the $5d^{10}6s^0$ ground atomic state to other states of higher valency.

AMMONIA SYNTHESIS AND DECOMPOSITION

The catalytic synthesis of ammonia from elemental nitrogen and hydrogen, apart from its great industrial interest, is historically important in the development of heterogeneous catalysis. Research in this area has had a strong influence on the thinking of many investigators in catalysis. The synthesis reaction and the reverse reaction of ammonia decomposition provide examples in which the specificity of catalytic action is very evident.

Catalytic activity for ammonia synthesis is found in the metals of groups VI, VII, and VIII of the periodic table (Frankenburg, 1955). The activity of these metals is linked with their ability to activate the nitrogen molecule on adsorption, presumably with formation of chemisorbed nitrogen atoms. The strength of chemisorption of nitrogen must not be too great, however, since formation of a stable bond between the reactant and surface inhibits catalytic action. The heat of adsorption of nitrogen on metals decreases markedly in the direction of increasing atomic number from Group VA to Group VIII in the periodic table (Hayward and Trapnell, 1964), and metals to the right of Group $VIII_1$ have essentially no ability to chemisorb nitrogen. The Group $VIII_1$ metals iron, ruthenium, and osmium are therefore the metals which have the ability to chemisorb nitrogen weakly and are correspondingly the most active catalysts for ammonia synthesis. In considering metals to the left of Group VIA in the periodic table, it is apparent that the strength of bonding of nitrogen to the surface is too great for catalysis to occur effectively. It is known that these metals exhibit a much greater tendency toward formation of bulk nitrides than do the metals in Groups VIA, VIIA, and VIII. The active metals do not form bulk nitrides under ammonia synthesis conditions. The only catalysts of commercial interest for ammonia synthesis contain iron as the active component. The catalysts are generally promoted with an alkali metal and alumina, the former serving as an electronic promoter and the latter as a structural promoter. The synthesis reaction is generally conducted at a temperature of approximately 450°C at pressures of several hundred atmospheres. The rate limiting step in the reaction is believed to be the chemisorption of nitrogen (Ozaki et al., 1960).

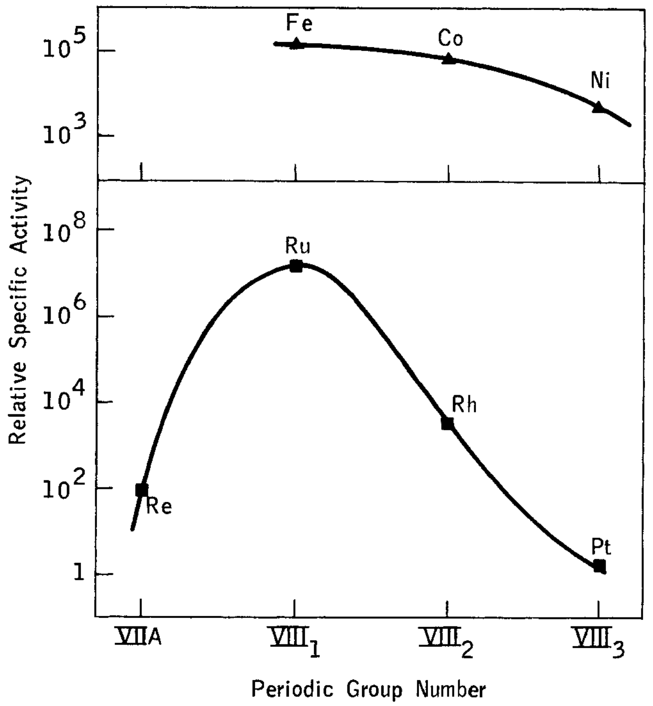

Fig. 7. Catalytic activities of evaporated metal films for ammonia decomposition at 400°C. The upper field in the figure gives activities of metals of the first transition series of the Periodic Table, while the lower field gives activities of metals of the second and third transition series [from data tabulated by Bond (1962b), which were derived from the paper of Logan and Kemball (1960)].

Because of the great practical importance of iron catalysts in ammonia synthesis, many fundamental kinetic investigations of the reaction have been conducted on iron. However, it is easier experimentally to investigate the kinetics of the reverse reaction of ammonia decomposition. Consequently, kinetic studies on other metals have generally been conducted on the latter reaction. Therefore, more data comparing the specific catalytic activities of metals are available for the decomposition reaction than for the synthesis reaction. A comparison of the specific activities of evaporated metal films for ammonia decomposition is given in Figure 7 plotted from data tabulated by Bond (1962), which were in turn derived from a paper by Logan and Kemball (1960). The upper field of the figure gives a comparison of iron, cobalt, and nickel in the first transition series of metals, while the lower field compares various metals within the second and third transition series. The Group $VIII_1$ metals, iron and ruthenium, are the most active. The pattern of variation of activity among the metals of the second and third transition series is very similar to that observed in the hydrogenolysis of ethane over these metals.

OXIDATION

Catalytic oxidation is another area of great practical interest. Important industrial reactions include the oxidation of sulfur dioxide and ammonia in the manufacture of sulfuric and nitric acids, respectively. Hydrocarbon oxidation reactions such as the oxidation of ethylene to ethylene oxide, propylene to acrolein, benzene to maleic anhydride, and naphthalene to phthalic anhydride are of great interest in the petrochemicals area. Recently, much attention has been given to the oxidation of carbon monoxide and unburned hydrocarbons in automobile exhaust gases as a result of the concern about air pollution.

The oxidation of hydrocarbons, particularly olefins, provides some striking examples of catalytic specificity. In general, paraffins are less reactive than olefins in oxidation and require more severe conditions for a given degree of conversion. As a result, the possibility of achieving selective partial oxidation reactions is poorer for paraffins. While selectivity is a general problem in hydrocarbon oxidation, there are several noteworthy examples of selective partial oxidation reactions of olefins which are of particular interest in a discussion of catalytic specificity. Therefore, the emphasis here will be on the oxidation of olefins.

A remarkable example of specificity in heterogeneous catalysis is the silver catalyzed oxidation of ethylene to ethylene oxide:

$$C_2H_4 + \tfrac{1}{2}O_2 \rightarrow C_2H_4O$$

The only known catalysts for the reaction contain silver as the active component. Moreover, ethylene is the only olefin which at present can be oxidized selectively to the epoxide by direct vapor phase reaction of olefin and oxygen over a solid catalyst (Voge and Adams, 1967). With other olefins on silver, the reaction is mainly one of complete oxidation to carbon dioxide and water. The oxidation of ethylene to ethylene oxide is conducted normally in excess oxygen at temperatures in the range of 200 to 300°C. In commercial practice, elevated pressures of 10 to 20 atm. are used, and the silver catalyst is commonly supported on a low surface area refractory oxide carrier such as alpha alumina. Electronegative elements such as the halogens are commonly employed as catalyst moderators to achieve optimum selectivity. Selectivities to ethylene oxide of 45 to 75% can be obtained with silver catalysts, depending on the type and amount of moderator used with the catalyst. The selectivity of a given catalyst is not a very sensitive function of conversion level or temperature. The reason for silver's unique ability to catalyze the epoxidation of ethylene has not been established. Much of the speculation on this matter has been concerned with the nature of the adsorbed oxygen which participates in the reaction. According to one commonly held view, the ability of silver to chemisorb oxygen nondissociatively, perhaps with formation of a surface peroxide (AgO_2), is important. Presumably, oxygen held on the surface in this form reacts readily with ethylene to form ethylene oxide, whereas adsorbed oxygen atoms react to form carbon dioxide and water. The failure of silver to catalyze the epoxidation of propylene and other olefins containing allylic hydrogen atoms is attributed to a competing mode of oxidation occurring by removal of a hydrogen atom at the allylic position in the molecule. In the case of propylene, the allylic hydrogen atoms are those in the CH_3 group. The C-H bonds in this group are 28 kcal/mole weaker than the C-H bonds in ethylene. The mode of oxidation occurring by hydrogen atom removal thus proceeds much more readily with propylene than with ethylene. In the case of silver catalysts this mode of oxidation leads to formation of carbon dioxide and water rather than partial oxidation products.

In contrast to silver catalysts, certain oxide catalysts, including cuprous oxide and bismuth molybdate, are effective for the selective partial oxidation of olefins containing allylic hydrogen atoms. Thus, on these catalysts propylene is oxidized selectively to acrolein:

$$CH_2{=}CH{-}CH_3 + O_2 \rightarrow CH_2{=}CH{-}CHO + H_2O$$

The reaction mechanism appears to involve the initial abstraction of an allylic hydrogen atom to form a symmetric allyl radical on the surface:

$$CH_2{=}CH{-}CH_3 \xrightarrow{-H} CH_2\overset{\frown}{\cdots}CH\overset{\frown}{\cdots}CH_2$$

The abstraction of a second hydrogen atom from either end of this intermediate then occurs, and this is followed by incorporation of oxygen to yield acrolein. While cuprous oxide and bismuth molybdate catalysts both give acrolein in the partial oxidation of propylene, they give different products in the oxidation of many C_4 and higher carbon number olefins. On cuprous oxide these olefins give aldehydes and ketones as the primary products, while on bismuth molybdate catalysts the major products are usually diolefins.

The Group VIII metals are active catalysts for the oxidation of olefins, but the major reaction is complete oxidation to carbon dioxide and water, as shown by studies on metal films (Patterson and Kemball, 1963). In the oxidation of ethylene and propylene on platinum, palladium, rhodium, gold, and tungsten films, the order of activities for oxidation is Pt>Pd>Rh>>Au>W. With the exception of gold, this order is the inverse of the order observed for heats of adsorption of oxygen. In the case of gold, there is a marked contrast with the transition metals, in that the chemisorption of oxygen does not occur readily on gold. Thus, we see again an example of catalytic activity increasing with decreasing strength of adsorption of a reactant to the point where adsorption of the reactant eventually becomes the limiting factor. On the Group VIA metal, tungsten, the oxygen is too strongly bound for high catalytic activity to result. As one proceeds from Group VIA to Group VIII, the strength of binding of the oxygen on the metal decreases, and the catalytic activity of the metal increases. On proceeding further to gold in Group IB, one finds that the ability to chemisorb oxygen now becomes the limiting factor, and catalytic activity decreases. Of the noble metals within Group VIII, platinum and palladium are the most active, as shown by the results of a study by Cant and Hall (1970) on the oxidation of ethylene and propylene. These workers employed silica-supported metals as catalysts. Specific activities taken from

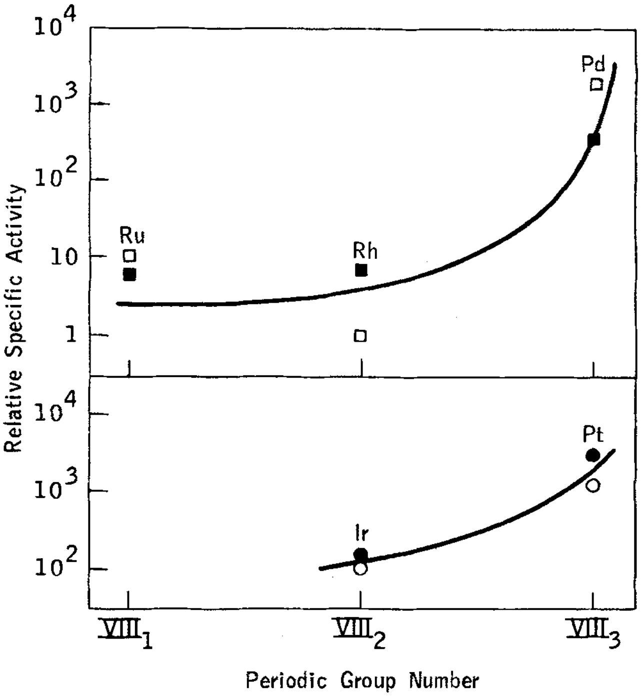

Fig. 8. Relative activities of Group VIII noble metals for the oxidation of ethylene at 130°C (open points) and propylene at 150°C (closed points). The two fields separate the noble metals of the second and third transition series (Cant and Hall, 1970).

their paper are shown in Figure 8 as a function of the position of the metal within the periodic table. The two fields in Figure 8 separate the Group VIII noble metals of the second and third transition series. The activities represent rates of complete oxidation of ethylene and propylene at 130° and 150°C, respectively. Oxidation activity increases in the direction of increasing atomic number across Group VIII. The pattern of variation of activity is the exact opposite of that found for the hydrogenolysis of ethane to methane (Sinfelt, 1969). Although complete oxidation to carbon dioxide and water was the predominant reaction, some partial oxidation products were observed. In the oxidation of ethylene, the partial oxidation products were acetaldehyde and acetic acid, with significant amounts (8 to 28%) being observed only with the palladium and iridium catalysts. In the oxidation of propylene, a variety of partial oxidation products was observed, including acrolein, acetone, C_3 acids, acetaldehyde, and acetic acid. Partial oxidation selectivities as high as 40% were reported by Cant and Hall in the oxidation of propylene on the ruthenium, rhodium, and iridium catalysts. The most active catalysts, platinum and palladium, were far less selective for the formation of partial oxidation products from propylene. The case of the iridium catalyst is especially interesting, since the partial oxidation reaction gave almost exclusively acetic acid as the product. The formation of acetic acid was also appreciable on the ruthenium catalyst, but not nearly so pronounced as on iridium. The high tendency toward formation of acetic acid on iridium, with the virtual exclusion of other partial oxidation products, indicates a high probability of cleavage of the double bond in propylene. This type of cleavage is somewhat unusual in partial oxidation, since the predominant products generally have the same number of carbon atoms as the olefin reactant. Studies by Cant and Hall (1972) on other olefins, including the butenes and pentenes, also show cleavage at the double bond in partial oxidation on iridium. Therefore, the reaction appears to be a fairly general one on iridium. Cant and Hall suggested that the particular activity of iridium for the double bond cleavage reaction may be associated with its ability to form coordination complexes with O_2. The reaction is visualized to proceed by addition of the double bond of the olefin across the coordinated oxygen molecule.

DECOMPOSITION OF ALCOHOLS AND ORGANIC ACIDS

Decomposition reactions of alcohols and organic acids proceed on both metallic and nonmetallic catalysts. In general, the nature of the decomposition depends on the type of catalyst. For example, the predominant reaction of alcohols on metals is usually dehydrogenation. Methanol decomposes to carbon monoxide and hydrogen, while ethanol and higher alcohols dehydrogenate to form aldehydes and ketones. Formic acid undergoes predominantly dehydrogenation on metals to form carbon dioxide and hydrogen. On nonmetallic catalysts, usually oxides, the major reaction of alcohols may be either dehydrogenation or dehydration, depending on the particular catalyst. The same is true of formic acid. Dehydration products from alcohols are olefins or ethers. Formic acid dehydration yields carbon monoxide.

The dehydrogenation of formic acid has frequently been used as a test reaction for comparing the activities of metal catalysts. When activity is considered as a function of the heat of formation of the bulk formate of the metal, it is observed that the most active metals are those with formates of intermediate stability (Fahrenfort et al., 1960). At one extreme, when the heat of formation of the bulk formate is low as with gold and silver, the reaction is presumably limited by the adsorption step leading to formation of a surface formate. This situation corresponds to a surface that is only sparsely covered by formate so that the reaction is close to first order in formic acid. At the other extreme, on metals such as nickel or iron whose bulk formates have much higher heats of formation, the reaction is limited by the decomposition of a relatively stable surface formate. The metal is then fully covered by the formate so that the reaction is zero order in formic acid. Neither of these extremes corresponds to high activity for the dehydrogenation of formic acid. The highest activity is observed for the Group VIII metals, which represent an intermediate case with regard to the stability of the surface intermediate.

With oxide catalysts, formic acid and ethanol decomposition studies provide a similar picture with regard to dehydrogenation and dehydration activities. Thus, both reactants undergo predominantly dehydrogenation on magnesium oxide and zinc oxide, and dehydration on alumina, silica and titania. Dehydration activity has been attributed to protonic acid sites on the surface, the protons being bound to oxygen in surface hydroxyl groups. Those oxides which undergo dehydroxylation of the surface too readily on moderate heating (400 to 500°C) have few protonic acid sites and are likely to exhibit low activity for dehydration relative to dehydrogenation (Mars, 1960).

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