

A STUDY OF THE ROLE OF CARBONATE SUPPORTS
FOR RHODIUM CATALYST IN HYDROGENATION REACTIONS

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FOR RHODIUM CATALYST IN HYDROGENATION REACTIONS

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SUMMARY

This research studied the role of different carbonate supports in heterogeneous catalytic hydrogenation reactions with rhodium catalyst. In a heterogeneous hydrogenation reaction, both the hydrogen gas and the substrate must be adsorbed on the catalyst surface, activated, and then react. This process of adsorption is dependent upon the type of catalyst used, and is often affected by the support for the catalyst.

The function of the support with respect to the catalyst varies for individual cases. It may be useful because it provides a larger contact surface and it may influence the structural and physical properties of the metal or oxide deposited on it. It may also protect the metal or oxide from poisons and hinders aggregation to preserve the fine dispersion of the catalyst. The selectivity of the catalyst as well as its activity may also be influenced by the nature of the support. It is the purpose of this research to study the role of calcium carbonate, nickel carbonate, cobalt carbonate, zinc carbonate, and cadmium carbonate as support for rhodium metal in catalytic heterogeneous hydrogenation reactions. Copper carbonate, though not used extensively, was also examined.

The catalysts were prepared by suspending the support in a solution of rhodium chloride and then reducing the salt to the metal. Three different reducing agents were used: namely, formaldehyde solution, hydrogen gas, and sodium borohydride. It was found that catalysts prepared with sodium borohydride reduction method were the most active.

The catalysts prepared were used in the hydrogenation of different functional groups of organic compounds. All the catalysts were found to be efficient in the hydrogenation of olefinic double bonds--5% Rh/NiCO₃ and 5% Rh/CoCO₃ were more effective than the others. When 5% Rh/ZnCO₃ was used in the hydrogenation of olefinic double bond, the activity was sharply decreased if there was a carboxylic acid group adjacent to the double bond.

When used in the reduction of the nitro group, all the catalysts were moderately effective except 5% Rh/CdCO₃ which showed exceptional efficiency in the hydrogenation of the nitro group.

The aromatic ring could be hydrogenated by using any of the catalysts prepared except 5% Rh/ZnCO₃; however, the rate was much slower than that for an olefinic double bond. On the other hand, 5% Rh/ZnCO₃ would be useful in selective hydrogenation of other functional groups in the presence of aromatic rings.

All the catalysts were found to be inactive towards the hydrogenation of carbonyl functions. A selective hydrogenation of carbon-carbon double bond was able to be obtained in such α,β -unsaturated compounds as crotonaldehyde. The role played by the carbonate supports in these hydrogenation reactions with rhodium catalysts was not entirely clear. In general, the catalysts behaved "normally" and reduced the more readily reducible functional group as expected. Surface areas were determined for these catalysts and it was observed that no correlation existed between the surface area of the catalyst and its activity; in other words, the hydrogenations were structure insensitive.

CHAPTER I

INTRODUCTION

Catalytic hydrogenation is a process by which certain metals, in finely divided form or dispersed on supports or carriers, induce reaction to take place on their surface. In order for reaction to occur successfully, the catalyst must have the ability to adsorb and to activate both the compound and hydrogen. It must also have the capacity to hold the molecules in a proper spatial relationship to the hydrogen. Finally, it is necessary, after reaction has occurred, for the resultant product to be desorbed or removed readily from the catalyst surface. This process is heterogeneous--that is, gaseous and liquid reactants interacting on the the surface of the solid catalyst. In catalytic hydrogenation, the system could then be considered as one composed of the solid catalyst and a hydrogen acceptor in a solvent surrounded by an atmosphere of hydrogen gas. In order for the hydrogen to contact the catalyst, it would be necessary for it to dissolve in the solvent and diffuse to the catalyst. To facilitate this, the entire mixture is agitated rapidly to minimize the slow diffusion process. Thus, both the hydrogen and acceptor molecules in contact with the catalyst surface may be adsorbed, activated, and then react. Desorption of product should occur immediately so as to present a "clean" catalyst surface upon which more reactant molecules can be adsorbed. Therefore, one must view the process of adsorption as of major significance in the catalytic hydrogenation process.

There are two types of adsorptions--physical adsorption and chemisorption. Physical adsorption is due to van der Waal's forces. It is essentially nonspecific with respect to adsorbent and adsorbate, easily reversible, and involves relatively small heats of adsorption.⁽¹⁾ Chemisorption, or activated adsorption, on the other hand, is the result of binding by valence forces of the same nature as those which bind atoms together in molecules.⁽²⁾ These forces are much stronger than those involved in physical adsorption, being on the order of 10 to 100 Kcal per mole, whereas physical adsorption are frequently found to be on the order of a few hundred calories per mole. In general, chemisorption is irreversible or is reversible only with difficulty, and is more selective than physical adsorption.

A number of other special features of chemisorption have to be considered, since they are of great importance in connection with the kinetics of surface reactions. The first is that after the surface has become covered with a single layer of adsorbed molecules, it is essentially saturated so that additional chemisorption cannot take place. This was verified by the work of J. K. Roberts,⁽³⁾ who found that the number of hydrogen molecules that could be adsorbed on a tungsten surface was 4.4×10^{14} per sq. cm. Assuming that hydrogen is adsorbed atomically, one atom being attached to each surface tungsten atom, the number of atoms adsorbed is 8.8×10^{14} which is very close to the number of surface tungsten atoms calculated to be $5.5 - 7.8 \times 10^{14}$ per sq. cm. The second feature is that the process of chemisorption may often have an appreciable activation energy, and hence may sometimes be a slow process. In some instances, particularly on oxide surfaces, the energies

of activation are relatively high and adsorption at low temperature takes place very slowly. The third feature is that there is frequently a considerable variation in the adsorptive capacities of the various surface sites. It has been suggested that adsorptions and chemical reactions occur predominately on certain "active sites" on the surface of the catalyst and that these sites are constantly being created and destroyed with the movement of excited electrons in the lattice.⁽⁴⁾ Chemisorption, therefore, plays a major role in surface catalysis of reactions of stable molecules. In view of the magnitude of the energy changes in chemisorption, the reactivities of molecules may be greatly changed or even markedly increased upon adsorption. Very often chemisorption is associated with dissociation of the adsorbed molecules, and the resulting adsorbed atoms are considerably more reactive. This is particularly true in the adsorption of hydrogen molecules on metal surfaces.

A number of catalyst systems have been used for hydrogenation reactions. The choice of a catalyst is usually governed by two factors: the activity and the selectivity required. The activity of a hydrogenation catalyst is a measure of the ease with which it catalyzes a given reaction, whereas, its selectivity can be defined as its ability to promote the hydrogenation of one functional group in a molecule in preference to any other reactive entities which may be present in that molecule.

One may divide metal catalysts into two types: supported or unsupported types. Unsupported metal catalysts are those used in the form of finely divided metal or the metal oxide.⁽⁵⁾ The metals are

referred to as blacks, and if dispersed and stabilized by substances such as gum arabic or polyvinyl alcohol, are termed colloidal catalysts. Support metal catalysts are those in which the metal or its oxides is deposited upon a suitable material of desirable stability. A variety of materials including such diverse substances as carbon, alumina, silica, alkaline earth carbonates and sulfates, metal oxides, asbestos, silk, etc., has been used as supports of metal catalysts.

The mechanical function of the support is to act as a base or framework for the catalytic component. It may serve to reduce shrinkage and lend physical strength. Aside from its purely mechanical function, other possible desirable effects of a support include the following:

1. It gives a larger exposed surface of active agents and thereby greater catalytic activity in case this agent by itself has low surface area; or gives an equal surface area and activity with much less active material. The latter is particularly important with expensive agents such as platinum metals.

2. It increases catalytic stability by keeping fine crystals of the active constituent too far apart for sintering to occur. Nickel catalysis were prepared by two different methods:⁽⁶⁾

- (a) from basic Ni carbonate reduced at 450° in hydrogen,
- (b) from basic Ni carbonate on inorganic supports (such as various common hydrosilicates of Al and Mg, decoloring charcoal, etc.) reduced at 450° in hydrogen.

These were then used in the hydrogenation of cinnamic acid. The activity of the latter catalyst was found to be much greater than the former.

This was attributed to the fact that the high temperature at which the

catalysts were prepared changed the surface of the individual particles of the catalyst so that there remained only a few points on these particles which are capable of adding hydrogen and acting as a carrier of it whereas the presence of inorganic skeleton hindered this change on the surface of the catalyst.

3. The support may increase adsorption as well as increase the surface contact of the catalyst.⁽⁷⁾ Unless a certain concentration of active molecules is present on the catalyst surface and favorable conditions for activation exists, no catalytic reaction can take place. There are places of different activity or centers of increased activity on the catalyzing surface consisting of weakly attached atoms, in which the reacting components are adsorbed exclusively. The deciding factors for the activity of the catalyst surface are the distances between active points which are located on corners and edges of crystals. Since these points are isolated atoms or molecules, they are less saturated by bonds of neighboring atoms than those located on the faces of crystals; therefore, they are in a state of freedom which is necessary for the catalyzing action. The deposition of a catalyst on a support may amount to an increase in the number of these active centers, corresponding to an energy level necessary to carry out a particular reaction.

4. The increase of active surface resulting from use of the support may result in a decrease in sensitivity to poisons. Maxted and co-workers⁽⁸⁾ have confirmed by experiment that in hydrogenation with platinum catalysts poisoned with dimethylsulfide the sensitivity to catalyst poisoning is inversely proportional to the surface area.

5. It is also reasonable to believe that a support exerts a

distorting action on the electric fields of the catalyst's active centers, changing thereby their sorptive ability toward not only hydrogen and acceptor molecules, but also to those other molecules present that ordinarily might poison the catalyst surface.⁽⁷⁾

6. The supported catalysts provide much more economical use of the metal. For example, hydrogenation of heptaldehyde proceeded eight times more rapidly over an equal weight (on a metal basis) of 5% platinum-on-carbon than that over platinum oxide.⁽⁹⁾

The relationship between performance of the catalyst and its support is extremely complex for, among other things, performance is related to the particular sample of support examined, to the precise method of metal deposition, and to the system in which the catalyst is used. There are many examples in the literature covering a variety of reactions in which one catalyst support is preferred to another. Unfortunately, observations on the effect of supports for the most part are incidental and are isolated instances. Some few attempts have been made to study the role of supports in hydrogenation reaction.

Maxted and co-workers⁽¹⁰⁾ have made a series of studies on the role of supports in catalytic hydrogenation emphasizing various oxide supports. They prepared a series of catalysts by depositing a fixed amount of platinum on varying amounts of different supports such as MgO, $\text{ThO}_2 \cdot 2\text{CrO}_3$, CeO_2 , Cr_2O_3 , ThO_2 , and ZrO_2 . The activity of these catalysts was then tested at 20°C and at atmospheric pressure, for the liquid phase hydrogenation of cyclohexene in absolute alcohol in a mechanically driven hydrogenation shaker operating under standardized conditions. The hydrogen uptake was found to be approximately linear

and therefore the volume of hydrogen absorbed in the first four minutes of hydrogenation was taken as a measure of the activity of the catalyst. By plotting these activities of the catalysts against the amount of support used (with fixed amount of platinum), they observed that with an increasing amount of each support, the activity first rises to a well-defined peak and then falls. These peaks occur at characteristically different catalyst-to-support ratio for each support. The surface areas of the supports were determined by the Brunauer-Emmett-Teller method and there was no direct correspondence between the surface areas of these supports and their effectiveness. The influence of the area of the support was shown with another set of experiments. They measured the activities of another series of catalysts in which varying amounts of platinum were deposited on a fixed amount of the same support. The results showed that as the amount of platinum dispersed on the support was increased, a slow rise in the rate of hydrogenation occurred, followed by a very rapid rise, and finally by a slower rise, apparently to a limiting value. They explained this phenomena by stating that, in the initial stages, the very small amounts of platinum were too sparsely distributed on certain areas of the surface of the support for the two points adsorption of cyclohexenes to occur in the manner postulated by Twigg and Rideal⁽¹¹⁾ for ethylene derivatives. However, as the amount of platinum was increased, the surface of the support became covered by platinum particles at a density more favorable for the necessary two-point adsorption of cyclohexene, and a relatively rapid increase in the hydrogenation rate occurred. Further addition of platinum resulted in unnecessary crowding of the platinum particles

with no significant change in cyclohexene adsorption. The hydrogenation rate thus rose more slowly to a limiting value.

In a later work,^(12,13) the same investigators have shown that the difference in activity for the hydrogenation of cyclohexene and of ethyl crotonate was dependent on the mean pore radius of the support as well as the nature of the support. Using essentially the same method, they compared the effect of zirconia, chromium sesquioxide, and alumina as supports for platinum catalyst in the hydrogenation of cyclohexene and ethyl crotonate. They postulated that when a metal was deposited on a porous support, some of the active surface becomes unavailable for catalysis by being contained in pores. The diffusion of reactant or resulting molecules to or from the active surface will be inhibited to different degree according to the size and shape of the pores and of the absorbable molecule. The use of a carrier with small pores to support the platinum would be expected to lead to a decrease in activity compared with that of the same amount of platinum of equal surface area deposited on a nonporous support, owing to the unavailability to a large molecule of part of the internal catalyst surface. The extent of the decrease in activity became greater the smaller the mean pore radius and the larger the unsaturated molecule to be hydrogenated. Their result showed that while zirconia and alumina had almost the same activity for the hydrogenation of cyclohexene, yet for the corresponding hydrogenation of ethyl crotonate, there is a wide difference in their activities. It was evident that the two supports were equally active for the hydrogenation of the smaller molecule, and that the fine pore structure of alumina (mean pore radius = 21 Å) was the cause of its relatively lower activity

compared with that of zirconia (mean pore radius = 382 \AA) for the hydrogenation of the more bulky molecule of ethyl crotonate.

Taylor and Staffin⁽¹⁴⁾ have studied the effect of the support at low metal levels on the kinetics of the hydrogenation of benzene to cyclohexane over a series of nickel catalysts. Briefly, the catalysts were prepared similarly by impregnating the support with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, after which they were dried overnight at 105°C , pressed into wafers, crushed, and then screened to a 45-60 mesh fraction. Two different supports, silica and silica-alumina, were used and the nickel concentration was varied in the 1-10% range. Kinetic studies were made in a differential flow reactor at temperatures in the range $70\text{-}200^\circ\text{C}$. The nickel surface areas of the catalysts were determined by hydrogen chemisorption. For benzene hydrogenation, there was little difference in specific activity between the 10% nickel catalysts. At lower concentrations, the nickel supported on silica-alumina was less active per square meter of nickel surface than that supported on silica. The difference between the specific activity of the nickel on the two supports increased as the metal level decreased, suggesting that the effect of the support is strongest at lower metal levels. It was suggested that the results are a consequence of an interaction of the metal with the support. The first increments of nickel impregnated on the surface of the support could selectively interact with the most energetic sites on the surface. Such an interaction could well be most pronounced at low nickel concentration, thus resulting in bigger difference in activity of the catalysts depending on the supports.

A study on the effect of support on the cis-trans isomer ratio

in dimethylcyclohexanes derived by hydrogenation of xylenes was made by Rylander and co-workers.⁽¹⁵⁾ All hydrogenations were carried out at 50 p.s.i.g. and at room temperature. Without exception, carbon-supported Rh or Ru catalysts gave less trans isomers than those metals on non-carbon supports such as BaCO_3 , BaSO_4 , SrCO_3 , and Al_2O_3 . They suggested that this might be due to a lesser tendency of olefinic intermediates to desorb from the carbon support.

Koch⁽¹⁶⁾ has shown that 5% ruthenium-on-carbon was more effective than 5% ruthenium-on-calcium carbonate in the hydrogenation of acetone and methyl ethyl ketone, but the reverse was true for the hydrogenation of heptaldehyde, cyclohexanone and levulose.

For the hydrogenation of cinnamaldehyde, Rylander and Himelstein⁽¹⁷⁾ stated that the support is an important factor in determining the selectivity; however, a correlation between the type of support, rate of reduction, and selectivity is not evident. When cinnamaldehyde was hydrogenated in methanol at room temperature and atmospheric pressure with 5% palladium on charcoal, only 50% hydrocinnamaldehyde was obtained; whereas, the same reaction was run using 5% palladium-on-barium sulfate as catalyst, 96% hydrocinnamaldehyde was obtained.

In general, supported catalysts have a number of advantages over unsupported ones. It is difficult, however, to assess the effect of supports without an intensive study involving pure substrates, pure solvents, and a standard method of depositing the particular metal on the various supports. Even then, there is the added factors of the relative acidity or basicity of the support, the particle size, total surface area, etc., that may affect the performance of the catalyst

which makes the study of the role of supports even more difficult.

One of the very important additions to the field of hydrogenation was the appearance of rhodium in its various catalytic forms. By far its greatest value is its ability to foster hydrogenation of aromatic systems to the corresponding cyclic and heterocyclic compounds at low pressure, often in the absence of acidic media. It is generally considered to be more difficult to hydrogenate the ring of homocyclic and heterocyclic compounds than it is to hydrogenate unsaturated open chain compounds, nitro groups, aldehydes, ketones, etc. Ring hydrogenations usually require the use of highly active catalysts at elevated temperatures and moderately high pressures of hydrogen. It was discovered⁽¹⁸⁾ that ring compounds may be speedily hydrogenated with gaseous hydrogen to their corresponding saturated cyclic compounds under normal conditions of temperature and pressure with the use of catalysts comprising of rhodium supported on a suitable carrier such as activated alumina or activated carbon. Reductions using rhodium catalysts have been found to be about 7 to 8 times faster than those with platinum dioxide under the same conditions for the hydrogenation of aromatic compounds, such as benzene, toluene, benzoic acid, phthalic acid, furan, and furoic acids. For compounds containing hydroxyl groups like phenol, resorcinol, and hydroquinone, the activity of the rhodium catalysts is in some cases from 16 to 30 times greater than with platinum catalysts.

Gilman and Cohn⁽¹⁹⁾ have studied the rate of hydrogenation of benzene with 5% rhodium-on-activated alumina or activated charcoal and the influence of substitution of alkyl-, hydroxyl-, and carboxyl groups on the benzene ring. All substitutions decreased the rate of

hydrogenation. The hydrogenation was stoichiometric, and no indication for cleavage of the groups substituted from the ring had been found. This is another important advantage rhodium has over platinum and other catalysts used for this purpose. They also found that rhodium-on-alumina catalyst was very effective in the hydrogenation of heterocyclic compounds such as pyridine, pyrrole, dimethyl furan, and furoic acid. They were able to reduce pyrrole to pyrrolidine in 97% yield very rapidly; such hydrogenation with platinum is very slow.

A study of the catalytic hydrogenation of methoxybenzenes over platinum and rhodium catalysts was made by Smith and Thompson.⁽²⁰⁾ Hydrogenolysis became a major factor in the reaction with platinum oxide, while with rhodium-on-alumina it is only a minor one in most cases. For example, at 30°C, 40-60% of the methoxy groups were cleaved under the influence of platinum oxide; 6-18% were cleaved under the influence of rhodium-on-alumina. The amount of cleavage increased linearly with temperature for all compounds except in the case of anisole. The fact that with the rhodium catalysts, particularly at lower temperatures, the aromatic nucleus was reduced with only slight cleavage of methoxy groups suggests again the very useful role these catalysts can play in organic syntheses.

Most catalysts that might be employed in the hydrogenation of compounds containing benzyloxy group promote hydrogenolysis to such an extent that their activity toward ring hydrogenation was considered to be of questionable synthetic value. It was later found that by using 5% rhodium-on-alumina as catalysts, the hydrogenation of several representative α substituted benzyl alcohols and benzyl ethers proceeds

rapidly and smoothly at room temperature and a pressure of 3-4 atmospheres of hydrogen to produce the cyclohexyl analogs in satisfactory yield.⁽²¹⁾

Alkoxyanilines could also be reduced to their corresponding alkoxy-cyclohexylamine with 5% rhodium-on-alumina at 60°C and 3.5 atmosphere initial hydrogen pressure.⁽²²⁾ The yield was respectable and hydrogenolysis was not extensive. Also, secondary amine formation in most instances was at a low level.

Cyclohexyl phosphonic acid can be prepared by various methods such as the reaction of cyclohexyl tosylate with the corresponding phosphite;⁽²³⁾ however, none of the methods is as convenient as the hydrogenation of the readily available aromatic compounds. By using rhodium-on-alumina catalyst, Freedman and coworkers⁽²⁴⁾ have been able to reduce aryl phosphonic and diarylphosphinic acids to the corresponding cyclohexyl compounds in a variety of solvents at room temperature and an initial hydrogen pressure of about 4 atmospheres. Halogen substituted phosphonic acids, however, suffered dehalogenation in this reduction.

The presence of acid is required when Adam's catalyst is used to convert pyridines to piperidines. Ruthenium dioxide gives excellent results in the hydrogenation of pyridines except it requires pressure in the range of seventy atmospheres. Hydrogenation of pyridines was successfully carried out in the presence of a 40% ratio of rhodium-on-carbon to pyridines at 55-60°C and 2.7 atmospheres initial pressure.⁽²⁵⁾

Rhodium-on-carbon has been used successfully to reduced carbon-carbon double bonds in α,β and β,γ unsaturated acids.⁽²⁶⁾ It was also

used to reduce nitrobenzene smoothly to aniline; however, the rate is considerably slower than that in the reduction of carbon-carbon double bonds. No reduction products were obtained when 1-nitrobutane and 2-nitropropane were hydrogenated to the corresponding amine with 5% rhodium-on-carbon as catalyst.

In the hydrogenation of benzonitrile with 5% rhodium-on-carbon as catalyst at room temperature and atmospheric pressure, dibenzylamine was the major product.⁽²⁷⁾ Using 5% rhodium-on-alumina as catalyst, a series of aliphatic nitriles were converted to the corresponding primary amines at room temperatures and in the presence of ammonia.⁽²⁷⁾

In addition to its uses in heterogeneous catalytic hydrogenation, more recently rhodium complexes have found extensive uses in homogeneous catalytic processes. While such catalysts and processes are quite different from those utilized in this research and will not be discussed here, suffice it to say that these catalysts, one of the more common ones being tris- (triphenylphosphine) rhodium chloride, are quite active and are potentially very useful in certain hydrogenation processes.

Small quantities of various substances have been incorporated in catalytic systems to alter their activities, selectivities, or catalyst life. Those having favorable effects are termed promoters and those with adverse effects are called inhibitors or poisons. Metals and metal salts have been used both as promoters and inhibitors.

Carothers and Adams⁽²⁸⁾ found that the addition of ferric chloride, as little as four parts per million, induced the reduction of benzaldehyde and heptaldehyde to proceed at a rapid rate in the presence of platinum oxide, in contrast to the extremely slow uptake of hydrogen in

the absence of this promoter. They also found that cobalt, manganese, and nickel acetates and chlorides had similar accelerating effects as the iron salts. Copper chloride had a slight inhibiting effect whereas copper acetate had a slight accelerating effect on this hydrogenation. Zinc acetate on the other hand completely suppressed the reaction.

Stannous chloride was reported to be the most effective promoter among a series of chlorides in the reduction of valeraldehyde with platinum oxide at room temperature and atmospheric pressure. Appreciable promotion with stannous chloride was also observed in the hydrogenation of ethyl cinnamate with platinum oxide; however, it had little effect when added to cyclohexene reduction. ⁽²⁹⁾

Rylander and Kaplan ⁽⁹⁾ noted that stannous chloride promoted the reduction of heptaldehyde with 5% palladium-on-carbon as well as platinum oxide. The addition of it to the reduction in the presence of ruthenium-on-carbon eliminated the long induction period often seen in reduction with ruthenium.

The addition of ferric chloride, ferrous chloride, or ferric hydroxide in a 1:1 ratio of iron to noble metal resulted in a 400% increase of hydrogen absorption per minute in the hydrogenation of nitrobenzene to aniline with palladium or platinum-palladium catalysts. ⁽³⁰⁾

Maxted and Marsden ⁽³¹⁾ investigated the effect of various metallic ions towards platinum in catalytic hydrogenation of crotonic acid at room temperature and normal pressure. The metals were added in the form of acetates and the results showed that mercury, bismuth, lead, tin, zinc, cadmium, aluminum, iron, nickel, and cobalt all deactivated palladium and platinum catalysts for the hydrogenation of crotonic acid.

Greenfield⁽³²⁾ studied the effect of a number of metallic salts on the palladium catalyzed reduction of p-nitrotoluene. The reductions were carried out at room temperature and a hydrogen pressure of about 4 atmospheres with 5% palladium-on-carbon as catalyst. No inhibition was shown by ferrous chloride. The reaction time was increased about 1.5-fold by nickel nitrate, and about two-fold by ferric chloride, ferric nitrate, cobalt nitrate, and chromium nitrate. More severe inhibition was caused by zinc nitrate and complete poisoning was produced by cuprous chloride, cupric chloride, cupric nitrate and lead nitrate.

Very often metal salts are added to facilitate selective hydrogenation of one functional group over another. Tuley and Adams⁽³³⁾ pointed out that most of the substances used as promoters by Carothers and Adams⁽²⁸⁾ acted as poisons for the reduction of olefinic bond in the hydrogenation of cinnamaldehyde with platinum. In the presence of both Zn and Fe salts in the proper proportions cinnamaldehyde was reduced to pure cinnamyl alcohol and no more than 1 equivalent of hydrogen was absorbed.

Furfural could be selectively hydrogenated to furfuryl alcohol with platinum oxide as catalyst and in the presence of ferrous chloride.⁽³⁴⁾ Csuros and coworker⁽³⁵⁾ reported that a variety of α,β -unsaturated ketones were hydrogenated to the unsaturated alcohols using a colloidal palladium catalyst in the presence of ferrous sulfate and zinc acetate. Selective reduction of carbonyl group in α,β -unsaturated aldehydes was also accomplished with platinum oxide catalyst and the addition of zinc ion or ferrous ion.^(33,36,37) The selective hydrogenation of 4-hexen-1-yn-3-ol to 1, 4-hexadien-3-ol was accomplished by

adding 40% by weight of lead acetate to 5% palladium-on-calcium carbonate catalyst and the reduction carried out at 20°C and 25 p.s.i. in an autoclave.⁽³⁸⁾ Selective reduction of acetylene to ethylene was also achieved in derivatives of α -ethynyl- β -ionol with mixtures of palladium-on-carbon and palladium-on-calcium carbonate catalysts with zinc acetate and diethylamine added.⁽³⁹⁾

Sometimes metal or metal salts are incorporated into the catalytic system during the preparation of the catalysts. Nitrocyclohexane was converted to cyclohexanone oxime at 105° and 100 atmospheres with catalyst prepared from heating chloroplatinic acid, zinc nitrate, calcium nitrate, and ammonium chromate to 350°C.⁽⁴⁰⁾ Acetylenes were selectively hydrogenated in the presence of diolefins by using Pd-Cu or Pd-Cu-Cr catalysts.⁽⁴¹⁾

Metals, metal oxides, and carbonates can also be used as supports for catalysts. Paal and coworkers^(42,43) have examined platinum or palladium metal supported on finely divided other metals, or on the oxides or carbonates of these metals. The catalysts were prepared by digesting the cleaned metal in palladium chloride or chloroplatinic acid solution. They found that in general bismuth, mercury, lead, tin, zinc, cadmium, copper, aluminum, or iron deactivates the catalyst, but that palladium or platinum acted normally if supported on magnesium, nickel, or cobalt.

In light of these results in which so called "foreign" substances have been utilized in effecting changes of the activity of a given metal catalyst, it was deemed desirable to initiate a systematic study of the activity and selectivity of a series of rhodium supported catalysts

in which the support would be on insoluble metal carbonates. Not only would the preparation methods be investigated, but also would the ability of the catalyst to hydrogenate various functional groups be quantitatively studied. The ability to effect hydrogenation would be studied kinetically by following hydrogen uptake during the progress of the reaction. Product analysis, using mainly vapor phase chromatography, would also be carried out.

CHAPTER II

EXPERIMENTAL APPARATUS

Hydrogenation Equipment

The hydrogenation equipment used in this work was a series 3901 Parr Pressure Apparatus manufactured by Parr Instrument Company of Moline, Illinois. It consisted of a hydrogen tank of approximately 4 liters capacity connected to a reaction bottle through a two-way valve and a section of a high pressure rubber tubing. The reaction bottle, with capacity of 420 ml. when filled to the top, was placed in a holder affixed at the top to rigid supports and at the bottom to an eccentric wheel by a connecting rod. The wheel was driven by an electric motor, thus enabling the reaction bottle to oscillate back and forth through a 30-degree arc at a frequency of 230 cycles per minute. The hydrogen tank was equipped with a thermometer well on the outside and connected to a cylinder of commercial hydrogen through a two-way valve with a pressure gauge and rubber tubing. The gauge was an Ashcroft Laboratory Test Gauge graduated in 0.20 p.s.i. unit. The reaction bottle was also connected to a vacuum pump through a two-way valve and a trap consisting of four glass tubes, the first two of which were filled with anhydrous calcium chloride and the second two filled with potassium hydroxide pellets.

Gas Chromatograph

To determine purity of the organic compounds used in this research

and to ascertain the distribution of products obtained, gas chromatographic analysis was used. The apparatus, a Model 720 F and M gas chromatograph, was manufactured by the F and M Scientific Corporation, Avondale, Pennsylvania. It is a dual column, temperature programmed instrument.

The two most commonly used columns were (a) a 2-foot, 1/4-inch o.d. stainless steel column, packed with 60-80 mesh Chromasorb P coated with 10 percent silicone rubber SE 30; or (b) a 6-foot, 1/4-inch o.d. stainless steel column, packed with 80-100 mesh Chromasorb L and coated with 10 percent Carbowax 20-M. Usual conditions were: injection port temperature 275°C; detector temperature 280°; helium flow 65 ml/min.; and chart speed set at 4. Samples of 4-5 microliter size were injected by means of a 10-microliter syringe.

Distillation Apparatus

Distillations required in this work were carried out using three different fractionation assemblies:

(i) An annular teflon spinning band distillation column manufactured by Nester/Faust Manufacturing Corporation of Newark, Delaware. It consisted of a rotating spiral band (27 inches) which acted as the packing in the column. A nichrome heating jacket around the column compensated for any heat loss. Two valves were used in the still, one controlled reflux ratio and the other was connected to a vacuum system.

(ii) A Todd Precision Distillation assembly made by Todd Scientific Company of Springfield, Pennsylvania. A three-foot, one-half inch diameter Vigreux type glass column was used.

(iii) A simple Vigreux-type column, 6 inches long and 1/2 inch in diameter, was used to distill small quantities of samples.

Surface Area Measurement

Surface areas of the catalysts were measured with an Orr Surface Area-Pore Volume Analyzer, Model MIC-101, manufactured by Numinco Corporation of Apollo, Pennsylvania. It consisted, in essence, of (1) a seven-valve manifold through which were interconnected three sample holders; (2) an evacuation system consisting of a cold trap, a diffusion pump, and a mechanical pump; (3) a sensitive pressure indicator; (4) a variable volume space; (5) a low-pressure detector; and (6) an inlet for the gases helium and nitrogen.

Reagents

Solvents

Ethanol. Absolute ethanol (99+ percent) was obtained from U.S. Industrial Chemicals and used without any further treatment.

Acetic Acid. Glacial acetic acid (reagent A.C.S.) purchased from Fisher Scientific Company was redistilled through the Todd Apparatus at 116.0 - 116.5°C and atmospheric pressure.

Hydrogen. The hydrogen gas was supplied in cylinders by Air Products Company of Atlanta, Georgia, and was used without further purification.

Catalysts

Five percent Rhodium/Calcium Carbonate was a commercially available catalyst obtained from Engelhard Industries, Inc., of Newark, New Jersey, Lot C-2786. The other catalysts used were prepared by using

$\text{RhCl}_3 \cdot \text{XH}_2\text{O}$ manufactured by Matthey Bishop, Inc., of Malvern, Pennsylvania, Lot No. 31273 containing 40% rhodium and suitable carbonates of certified A.C.S. grade.

All other chemicals necessary for hydrogenation were purchased as commercially available high-grade products and then redistilled or recrystallized before use.

Preparations

Preparation of Catalysts

Three different methods were employed in preparation of the catalysts for the hydrogenation reactions.

Reduction with Formaldehyde Solution.⁽⁴⁴⁾ In order to obtain 10 g samples of catalysts, 1.316 g of the RhCl_3 (40% Rh) was required. The rhodium chloride was weighed out to the nearest tenth of a milligram in a small cleaned beaker and then dissolved in 1.3 ml. of conc. HCl and 5 ml. of distilled water. This solution was added dropwise with a disposable pipette to a hot suspension (80°C) of 10 g of CaCO_3 (or other carbonate) in a 100-ml. of distilled water with constant stirring with a magnetic stirrer. After the suspension had become uniform in color, 1.2 ml. of a 37% formaldehyde solution was carefully added dropwise by means of a graduated pipette into the mixture with vigorous stirring. After continued stirring for an additional 5 minutes, the suspension was made slightly alkaline to litmus using a 30% sodium hydroxide solution, during which time constant stirring was maintained. The suspension was stirred for 5 more minutes and then the catalyst was allowed to settle. The clear supernatant liquid was decanted and replaced by distilled

water. The catalyst was resuspended by stirring and it was permitted to settle again, after which the supernatant liquid was decanted. These steps were repeated eight times. Following final decantation, the catalysts was collected by filtration on a 90-mm medium porosity sintered glass funnel. Most of the water was removed from the cake, but not enough to cause the cake to break or channel. The filter cake was washed with 250 ml. of distilled water in five portions, the last being removed as completely as possible by suction filtration. The funnel and its contents were then placed in an oven at 110°C overnight until the catalyst was thoroughly dry.

Reduction with Hydrogen Gas. To a solution of 1.316 g of RhCl_3 (40% Rh) in 100 ml. of distilled water contained in a Parr hydrogenation bottle, 10.0 g of CaCO_3 (or other carbonate) was added. Hydrogenation of the mixture utilizing the Parr apparatus at room temperature and an initial hydrogen pressure of 50 p.s.i. for 1.5 hours was effected. The catalyst was removed by filtration, washed with 300 ml. of distilled water in five portions and dried in air for about 30 minutes. Finally, it was placed in an oven at 110°C to dry overnight.

Reduction with Sodium Borohydride Solution.⁽⁴⁵⁾ A suspension of 10.0 g of CaCO_3 (or other carbonate) in 100 ml. distilled water was prepared in a 400-ml. beaker covered with a watch glass. A prepared solution of 1.316 g RhCl_3 (40% Rh) in 6 ml. of distilled water was added to the suspension dropwise with constant stirring at 25-27°C with a magnetic stirrer over a period of 2 minutes. Another 4 ml. of distilled water was used to rinse the small beaker which was used to hold the rhodium chloride solution, and this was also added to the suspension.

A solution of 0.1455 g NaBH_4 in 5 ml. of distilled water was prepared and was added with vigorous stirring over a period of 8 minutes into the suspension. Another 5 ml. of distilled water was used to rinse this small beaker and the wash was added to the suspension mixture. This entire mixture was stirred for an additional 5 minutes. When stirring was stopped, the suspension allowed to settle, following which the supernatant liquid was decanted. An equal volume of distilled water was added to the solid remaining and the catalyst was resuspended by stirring. Again, the solid was allowed to settle and the liquid decanted. These steps were repeated four more times. Collection of the catalyst by filtration through a 60-ml. medium porosity sintered glass funnel was effected. Washing of the residue with 300 ml. of distilled water in 50 ml. portions gave the catalyst which was then dried overnight in an oven at 110°C .

Preparation of Hydrogenation Equipment

All hydrogenation apparatus was cleaned very thoroughly in as much as the presence of small amounts of foreign material could possibly poison the catalyst system. Therefore, the hydrogen tank was evacuated and flushed with fresh hydrogen gas several times. All rubber tubing connections and all rubber stoppers were boiled first in strong sodium hydroxide solution for several hours to remove free sulfur and extractable sulfur compounds, then in tap water, and finally in distilled water prior to being used.

When not in use, the system was kept sealed at all times, and a constant hydrogen pressure was maintained within the system during this

time.

The reaction bottles were thoroughly cleaned with a brush using a synthetic detergent and tap water. This was followed by treatment with chromic acid cleaning solution, rinsing with tap water, and finally rinsing with distilled water. All the bottles were dried in an oven at 110°C and after cooling, were capped with aluminum foil until needed.

All other glassware used, such as graduated cylinders, pipettes and syringes were subjected to the same cleaning process.

Hydrogenation Procedure

The general method for hydrogenation was as follows. The desired amount of the catalyst was weighed to the nearest tenth of a milligram on a cleaned tared watch glass and then transferred into the reaction bottle by means of a small camel's hair brush. Fifty ml. of absolute ethanol was measured into the reaction bottle from a 100-ml. graduated cylinder. By means of a cleaned syringe for liquid samples or a camel's hair brush for solid samples, a 0.02-mole sample of the compound to be hydrogenated was then introduced to the reaction bottle. The bottle was then placed in the bottle holder and securely fastened. By proper use of the valves, the bottle was evacuated, filled with hydrogen, and then evacuated again. This cycle was repeated three times. Finally the bottle was filled with hydrogen again until the pressure of the whole system was to 50.0 p.s.i. as indicated by the pressure gauge. The whole system was allowed to stand for two to three minutes, while the atmospheric pressure and the room temperature were obtained and recorded. After the internal pressure of the system had reached equilibrium, the

reaction started when the electric motor powering the bottle shaking assembly was switched on. A timer was started and the gauge pressure determined simultaneously. The progress of the reaction was followed by noting pressure change as a function of time.

When the reaction was complete, the shaker and timer were stopped. The valve between the hydrogen reservoir and the reaction bottle was closed and the bottle was evacuated. The valve system to the bottle was then opened to atmosphere permitting air to enter the system. The bottle could then be removed from the holder with safety. The catalyst was removed by suction filtration from the reaction mixture using a medium porosity sintered glass filtering funnel. The reaction mixture was retained for v.p.c. analysis.

Surface Area Measurement

Surface areas of all catalysts were measured by means of the low-temperature gas adsorption method using the Orr Surface Area-Pore Volume Analyzer. This device utilizes the principle derived by Brunauer, Emmett, and Teller.^(46,47) The surface area was evaluated by determining the amount of gas necessary to form a single layer of gas molecules on the surface of the catalyst. This was accomplished with nitrogen gas at the temperature of liquid nitrogen (approximately -195°C), since under these conditions, the gas molecules are known to form a uniform, tightly packed layer. Thus if the space occupied by each nitrogen molecule was known within reasonable limits under this condition, the surface area of the catalyst can be ascertained.

Brunauer, Emmett, and Teller⁽⁴⁶⁾ have developed such an equation

and this has proved to be very useful in interpreting multilayer gas adsorption isotherms and thus yielding information as to the surface area of the catalyst. The equation could be expressed in the form of

$$\frac{x}{V(1-x)} = \frac{x^1}{V_m C} + \frac{(C-1)x}{V_m C}$$

where x is the relative pressure P/P_0 for the adsorbate, namely, nitrogen gas; V is the volume of gas (S.T.P.) adsorbed at relative pressure x ; V_m is the volume of adsorbate required to form a monolayer on the surface of the adsorbent; and C is a constant. A plot of the left-hand side of the equation against the relative pressure x yield a value for V_m and one for the constant C . Utilizing the fact that the cross-sectional molecular area of nitrogen gas at -195.8°C is 16.2\AA^2 , the specific area of the sample could be calculated.

The experimental procedure was described in detail in the instruction manual accompanying the analyzer. In general, the sample to be analyzed was weighed to the nearest tenth of a milligram in a cleaned dried sample tube. The sample was then degassed by applying heat to about 200°C and a good vacuum of less than 1 micron of mercury. A period of about 24 hours was considered necessary to degas the sample. Helium gas was used to obtain the unoccupied sample tube volume at liquid nitrogen temperature. After this, the sample was again degassed to remove the helium gas. After several hours, the adsorption test was performed using nitrogen gas. After admitting nitrogen into the sample tube (which was immersed in a Dewar flask containing liquid nitrogen), the initial and final pressure of the gas were recorded. This series

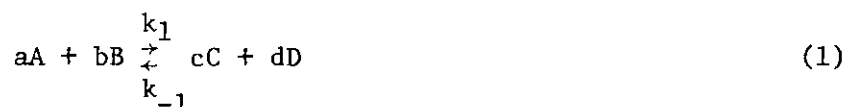
of steps was repeated three or four times. The ratio between the initial and final pressure was then plotted against the function $x/V(1-x)$ to obtain the surface area of the sample.

Kinetic Data Treatment

General Rate Behavior in Heterogeneous Catalytic Reactions

Since the experimentation involved in this research was also concerned with kinetics, it seems desirable to discuss the equations and terminology which will be used in later chapters of this thesis.

Consider an equilibrium reaction



where a, b, c, and d represent the requisite stoichiometric coefficients and A, B, C, and D the molecular formula; and k_1 and k_{-1} are the appropriate rate constants for the forward and reverse reactions. The rate of the reaction can be expressed in terms of the rate of disappearance of compound A

$$-\frac{d[A]}{dt} = k_1[A]^a[B]^b - k_{-1}[C]^c[D]^d \quad (2)$$

where [A], [B], etc., are molar concentrations and a, b, etc., are generally whole number exponents. In the case where the reverse reaction is negligible, the rate equation becomes:

$$-\frac{d[A]}{dt} = k_1[A]^a[B]^b \quad (3)$$

The number $n = a + b$ is known as the order of the reaction.

Smith and coworkers^(48,49) have shown that for a series of

catalytic hydrogenations, the reaction was zero order with respect to the substance being hydrogenated and first order with respect to the hydrogen pressure. Therefore, the rate equation for such hydrogenation reaction can be written as

$$-\frac{d[H_2]}{dt} = k_1 [H_2]^1 [B]^0 = k_1 [H_2] \quad (4)$$

where $[H_2]$ and $[B]$ represent the concentration of hydrogen gas and the compound being hydrogenated, respectively. Since in the actual experiment, the pressure and not the concentration of hydrogen is being measured as a function of time, it would be desirable to express the rate equation in terms of the pressure. From general gas relationships it can be stated that

$$[H_2] = ZP_H \quad (5)$$

where P_H is the absolute pressure of hydrogen and Z is a proportionality constant dependent on the volume of the system, the temperature of the gas, etc.

Substituting equation (5) in equation (4), one obtains

$$-\frac{d[ZP_H]}{dt} = k_1 ZP_H \quad (6)$$

or

$$-\frac{d[ZP_H]}{P_H} = k_1 Zdt \quad (7)$$

Upon integration of equation (7) between limits of $P_H = P_o$ at $t = 0$ and $P_H = P_t$ at $t = t$, one obtains

$$\log \frac{P_o}{P_t} = \frac{k_1 Z t}{2.303} \quad (8)$$

Thus plotting $\log P_o/P_t$ versus time will yield a straight line, the slope of which will be $k_1 Z/2.303$. Therefore, the apparent rate constant of the reaction $[k_1 Z]$ can be obtained by multiplying the slope of the line by 2.303.

CHAPTER III

DISCUSSION OF RESULTS

Methods of Preparation of Catalysts

Supported metal catalysts are prepared by variations of a few procedures, the object of which is to obtain metal or metal compounds in highly dispersed form. A frequently used procedure involves precipitation of the catalytic metal onto a support by converting a solution of the metal salt to the insoluble metal by some method of reduction while in the presence of the support. Mozingo⁽⁴⁴⁾ described the preparation of 5% palladium-on-barium sulfate, barium carbonate, or strontium carbonate in which palladium chloride is reduced to palladium by alkaline formaldehyde in the presence of the finely divided support. Hydrogen gas is often used as reducing agent, but other suitable reducing agents can be used, a few of which are hydrazine,⁽⁵⁰⁾ sodium formate,⁽⁵⁰⁾ and sodium borohydride.⁽⁴⁵⁾

During the course of this research, the catalysts were prepared utilizing three different reducing agents, namely, formaldehyde, hydrogen gas, or sodium borohydride. The effectiveness of these catalysts was tested in the reduction of different functional groups. The rates of hydrogenation is given in Table 1.

As the results show, sodium borohydride was the most efficient reducing agent of these for the preparation of catalysts, particularly in the cases of rhodium-on-nickel carbonate and rhodium-on-cadmium

Table 1. Rate of Hydrogenation With Catalysts Prepared by Different Methods

Catalyst	Compound	Rate, $K_1 \times 10^4 \text{ g}^{-1} \text{ min}^{-1}$		
		Formaldehyde Reduction	Hydrogen Gas Reduction	Sodium Borohydride Reduction
5% Rh/CaCO ₃	Cyclohexene	100	104	128
5% Rh/NiCO ₃	"	-	25	130
5% Rh/ZnCO ₃	"	55.5	83.1	88.8
5% Rh/CdCO ₃	"	too slow	38.2	105
5% Rh/NiCO ₃	Nitrobenzene	-	too slow	5.0
5% Rh/ZnCO ₃	"	-	0.8	1.0
5% Rh/CdCO ₃	"	-	too slow	11.0
5% Rh/NiCO ₃	Benzoic Acid	-	no rx.	1.4
5% Rh/ZnCO ₃	Crotonaldehyde	-	6.5	27

carbonate where there was a significant increase in the activity when sodium borohydride was used. Therefore, catalysts prepared by this method were used for the work discussed in the latter part of this chapter.

Reproducibility of Catalyst Preparations

The performance of a catalyst depends, among other things, on the way the catalyst is prepared. Different batches of catalysts may well have different activity even though they were presumably prepared under apparently identical conditions since all preparation are subjected to various subtle and often unknown influences that alter catalyst quality. During the course of this research, an initial effort was made to prepare a large enough batch of catalyst to last throughout this investigation.

However, when a second batch of catalyst became necessary, effort was taken to duplicate precisely every step in the preparation of that catalyst. Various factors such as the temperature, the rate of addition of reducing agent, the rate of mixing, the number of times of washing, the quantity of water used for washing, and the temperature and time for drying were all kept as consistent as possible. Catalysts from duplicate catalyst preparations were checked for their activity and selectivity. When two different batches of 5% rhodium-on-zinc carbonate, prepared by hydrogen gas reduction, were used in the hydrogenation of cyclohexene, the first batch yielded a rate constant of $77 \text{ g}^{-1} \text{ min}^{-1} \times 10^{-4}$ whereas the second batch gave a rate constant of $83 \text{ g}^{-1} \text{ min}^{-1} \times 10^{-4}$. The same experiment was performed with two batches of 5% rhodium-on-copper carbonate prepared by sodium borohydride reduction. In this case, the rate constant obtained when the first batch was used was $99.5 \text{ g}^{-1} \text{ min}^{-1} \times 10^{-4}$, and that from the second batch was $106.0 \text{ g}^{-1} \text{ min}^{-1} \times 10^{-4}$. Although the rate constants differ by about 6 percent in both instances, this is not inconsistent with results obtained when duplicate runs were made using the same batch of catalyst. Hydrogenation of cyclohexene with commercial 5% Rh/CaCO₃ yielded rate constants of $157 \text{ g}^{-1} \text{ min}^{-1} \times 10^{-4}$ and $150 \text{ g}^{-1} \text{ min}^{-1} \times 10^{-4}$ with about 5% difference. It shows that the reproducibility of runs from the same batch of catalysts is equivalent to the values obtained from different batches. Therefore, the precise method of preparation discussed in the previous chapter, if carefully followed, may be considered to be reliable for yielding reproducible batches of catalysts.

The Relationship Between the Reaction Rate
Constant and the Amount of Catalysts Used

The amount of catalyst used in a hydrogenation reaction obviously might be expected to affect the rate of that process quite possibly the product, and in commercial operations the economics of the process. Considering a heterogeneous reaction to be one occurring on the surface of the catalyst, it would be expected that the reaction rate would be proportional to the amount of that surface and, in turn, to the amount of catalyst present. This would be true, however, only over a certain range of the amount of catalyst. For this expectation to be true, it is necessary that the entire, total surface available for adsorption and reaction of reactants be utilized at each instant of time. Further, it is necessary that products, once formed, be desorbed so that the reactants surrounding the clean surface can be immediately re-adsorbed for reaction. In other words, the total surface is constantly being utilized for reaction in an equilibrated process until at least one reactant is consumed.

There are several factors or circumstances which can prevent reaction rate constants for heterogeneous hydrogenation reactions from being directly proportional to the amount of catalyst used over wide ranges of quantities of catalysts. The first of these, of major significance when quite small amounts are used, is that of surface poisoning. Poisoning may result from unintentional addition of minute quantities of substances which may be strongly adsorbed to the catalyst surface, thus preventing use of that surface for profitable reaction. It may also result from product not being desorbed rapidly enough, thus

decreasing the rate at which reactants adsorb and undergo reaction. Such effects wherein available surface is removed from possible use obviously would be noted more when the initial surface area was small since a greater percentage of that surface is affected by the poisoning process. The slowness of product desorption would have similar visible results as would catalyst fatigue and/or slight surface changes affecting the active sites of adsorption.

The second major factor would be observable more commonly when large amounts of catalyst were employed for a given amount of reactant. It could also be observed whenever a very rapid reaction occurs or when ineffective stirring or mixing is being utilized. In each of these one can visualize the catalyst covered by reactants and reaction followed by desorption occurring. If this happens so that insufficient reactants are in the liquid phase adjacent to the solid catalyst to cover the surface, then the surface is momentarily not being fully utilized. Reaction can occur only as reactants diffuse through the liquid and reach the surface. Hence the reaction rate is controlled by the rate of diffusion and will not be dependent upon the total catalyst surface.

Thus, for studies in which catalyst effectiveness is being considered as of major emphasis, it is necessary that the concepts of equilibria involving adsorption of and availability of reactants to a uniform total surface be a major criteria.

The rates of hydrogenation of 0.02 moles of cyclohexene and 0.02 mole of crotonaldehyde in ethanol over various amounts of 5% rhodium-on-calcium carbonate were shown in Table 2.

Figure 1 shows a plot of the rate constants versus the amount of

Table 2. Rates of Hydrogenation of Cyclohexene and Crotonaldehyde with 5% Rhodium-On-Calcium Carbonate

Weight of Catalyst	Rate $\times 10^4 \text{ g}^{-1} \text{ min}^{-1}$	
	Cyclohexene	Crotonaldehyde
0.5 g	432	-
1.0 g	331	36
1.5 g	220	-
2.0 g	180	34
3.0 g	120	-

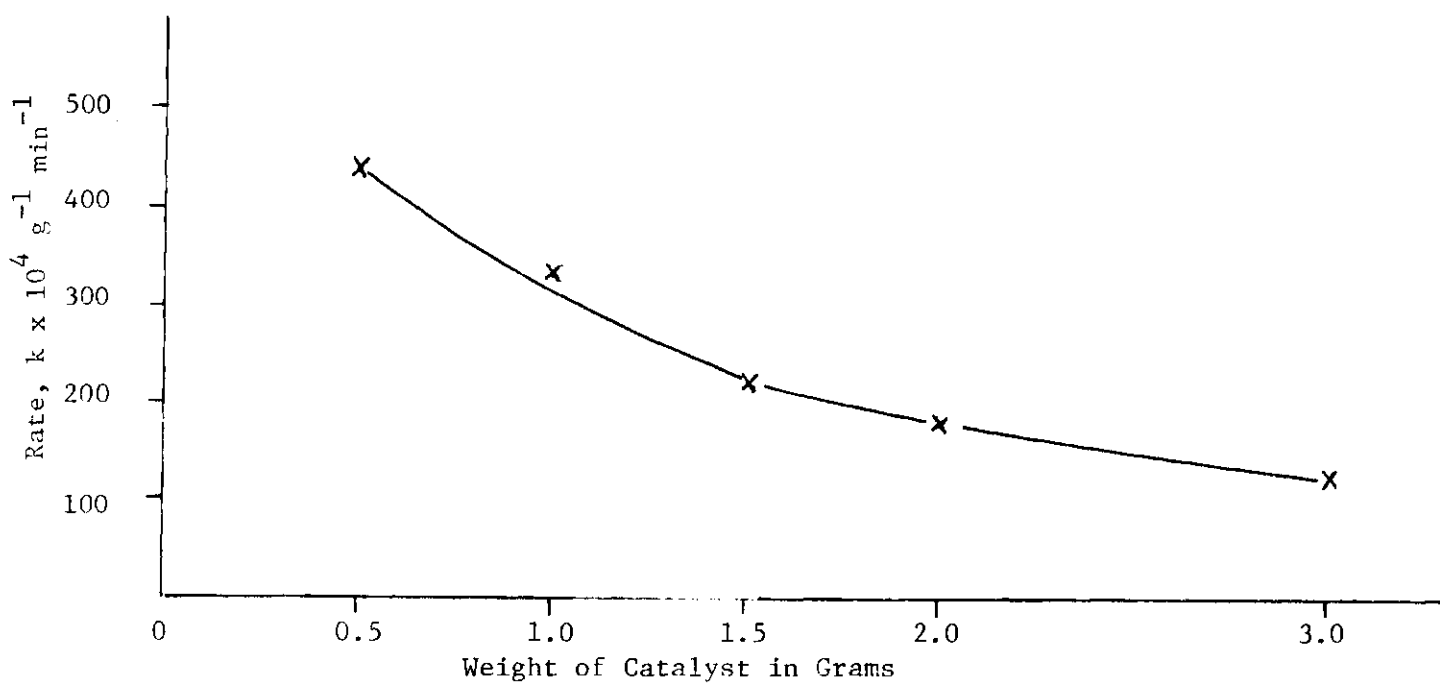


Figure 1. Rate Constants Versus Weight of Catalyst.

catalyst used. From the graph, we can see that the rate constant begins to level off noticeably when 2.0 g of catalyst was used. This means that an equilibrium is being established between adsorption and availability of reactants to the catalyst surface. During the course of this research, in order to obtain enough information at a reasonable amount of time and also run the hydrogenation reaction at close to equilibrium conditions, we chose to use 2.0 g of catalyst throughout this research. To have selected larger amounts would present a problem in that too few pressure readings could be taken in the short time during which reaction was occurring.

The Relationship Between the Reaction Rate Constant
and the Initial Hydrogen Pressure

The hydrogenation of cyclohexene and crotonaldehyde with commercial 5% rhodium-on-calcium carbonate were carried out at different initial hydrogen pressure. The results are tabulated in Table 3.

Table 3. Rate Constants Versus Initial Hydrogen Pressure

Initial Hydrogen Pressure	Cyclohexene Rate x 10 ⁴ g ⁻¹ min ⁻¹	Crotonaldehyde Rate x 10 ⁻⁴ g ⁻¹ min ⁻¹
64.3	153	55
32.3	145	67
16.0	218	-

Each of the reactions followed first order kinetics over the pressure drop noted in a single run since a plot of $\log P_o/P_t$ versus t (Eq. 8, Chapter 2, page 30) yielded a straight line. A typical plot of

this is shown in Figure 2. The relationship also appears valid over the larger pressure range of 32-64 psia as evidenced from the results cited in Table 3 which are within experimental deviation. At lower initial hydrogen pressures, there appears to be a slight change from the first order relationship.

Reduction of Olefins

The carbon-carbon double bond is very easily reduced. Successful reduction have been carried out over all the platinum metals in a variety of solvents and within a wide range of conditions. Only a few highly hindered olefins have been found resistant to hydrogenation.

All the catalysts prepared in this research were used to reduce simple alkenes, such as cyclohexene, successfully. Table 4 shows the results of the hydrogenation reaction of cyclohexene.

Table 4. Hydrogenation of Cyclohexene

Catalyst	Rate $\text{g}^{-1} \text{min}^{-1} \times 10^4$	Product
5% Rh/CaCO ₃ ^a	157	Cyclohexane
5% Rh/CaCO ₃ ^b	128	Cyclohexane
5% Rh/NiCO ₃ ^b	130	Cyclohexane
5% Rh/CoCO ₃ ^b	127	Cyclohexane
5% Rh/ZnCO ₃ ^b	88.8	Cyclohexane
5% Rh/CdCO ₃ ^b	105	Cyclohexane

^aThis catalyst was purchased from Engelhard Industries, Inc.

^bThese catalysts were prepared with NaBH₄ reduction method.

The reduction of cyclohexene using rhodium catalyst on different carbonate supports was a fast reaction. In most cases the reductions were complete within one minute and the products, as analyzed by gas chromatography, were within 95-100% yield. The reduction was first order with respect to hydrogen pressure. Figure 2 shows a plot of $\log P_o/P_t$ versus time indicating the first order relationship.

Hydrogenation of other olefinic compounds containing different reducible functional groups was also carried out. The results of these reductions are shown in Table 5, the rates indicated being based upon the initial two to three minutes of the hydrogenation. In all cases in Table 5, the rate refers to the hydrogenation of the carbon-carbon double bond only. In some cases, the compound might be further reduced if there is another reducible functional group present such as an aromatic ring. However, in every case except cinnamaldehyde, which will be discussed later, the olefinic double bond was reduced first, more rapidly than any other reducible group. If the reaction was stopped when one equivalent of hydrogen had been taken up, excellent yields of the olefinic-reduced compound were obtained. In the case of crotonaldehyde, a quantitative yield of n-butyraldehyde was obtained.

As the results indicate, the 5% Rh/CaCO₃ catalyst purchased commercially was generally superior over the other catalysts. The 5% Rh/CaCO₃ catalyst made with NaBH₄ reduction method is not as active as the commercial sample.

Rhodium-on-nickel carbonate and rhodium-on-cobalt carbonate catalysts showed about the same activity towards olefinic bonds though in most cases the nickel carbonate supported catalyst was slightly

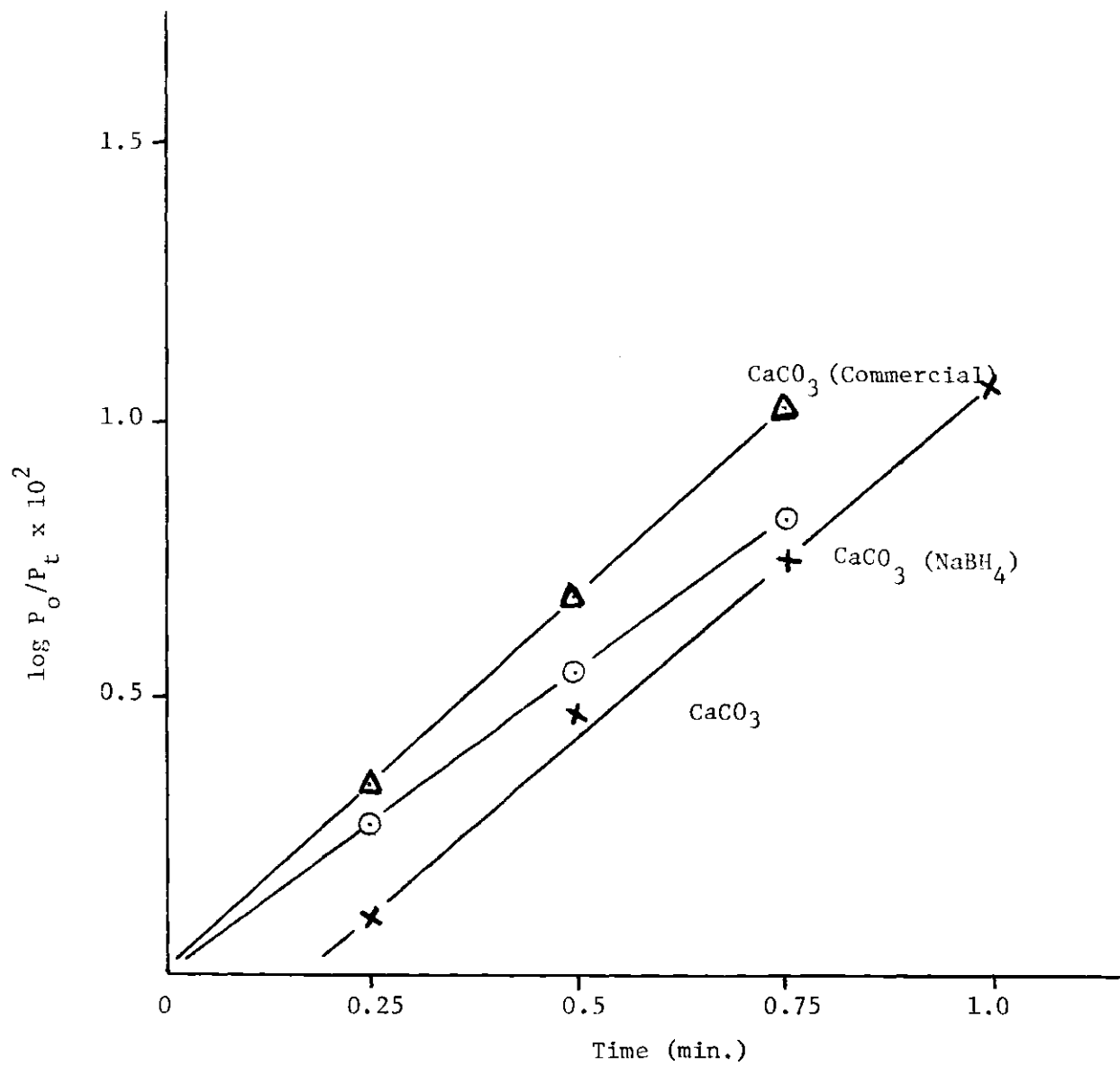


Figure 2(a). Hydrogenation of Cyclohexene.

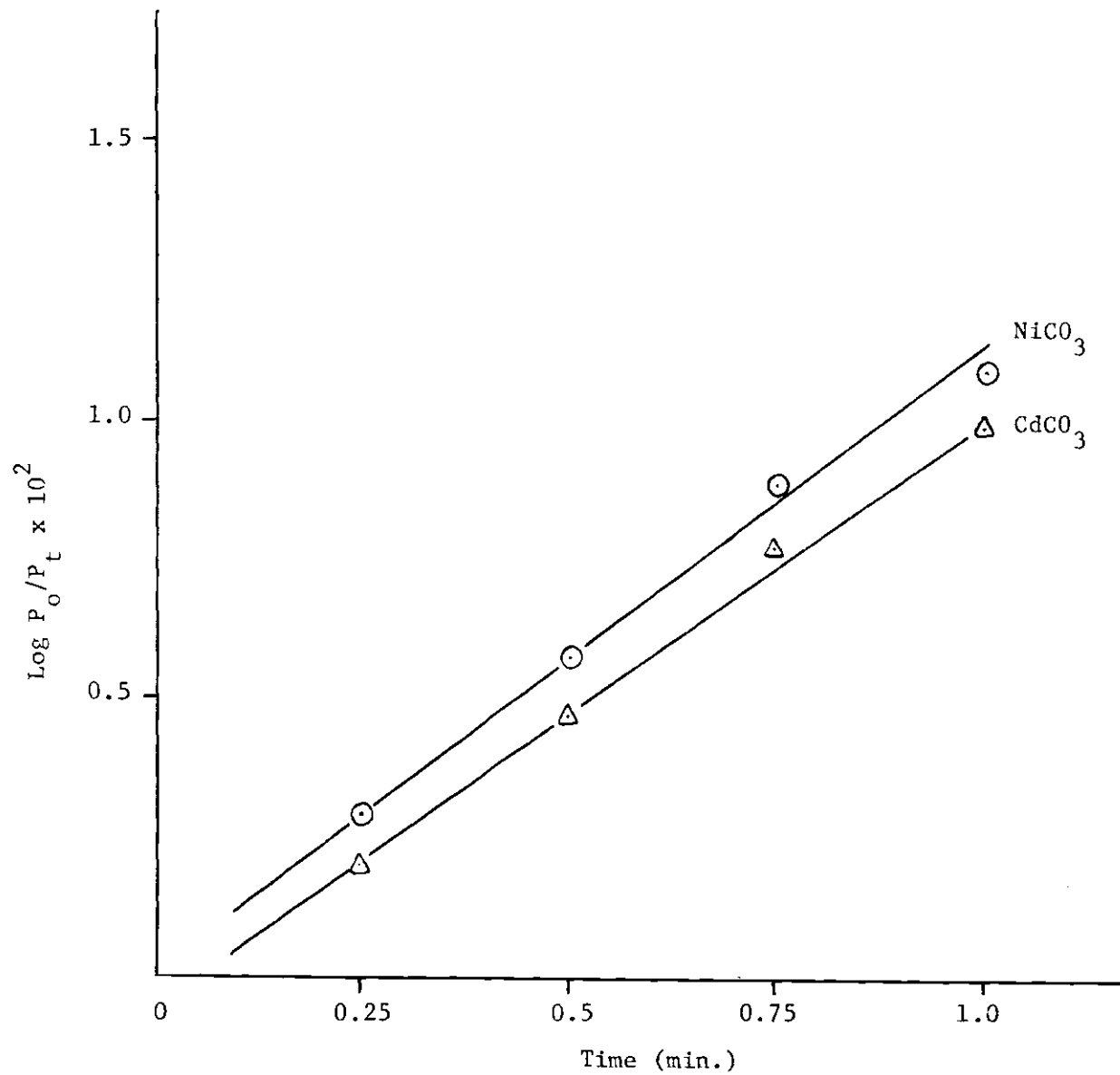


Figure 2(b). Hydrogenation of Cyclohexene.

Table 5. Hydrogenation of Alkenes

Compound	Catalyst	Product	Rate x 10 ⁴ g ⁻¹ min ⁻¹
Crotonic Acid	5% Rh/CaCO ₃ ^a	Butyric Acid	171
Crotonic Acid	5% Rh/CaCO ₃ ^b	Butyric Acid	99
Crotonic Acid	5% Rh/NiCO ₃ ^b	Butyric Acid	189
Crotonic Acid	5% Rh/CoCO ₃ ^b	Butyric Acid	167
Crotonic Acid	5% Rh/ZnCO ₃ ^b	Butyric Acid	26
Crotonic Acid	5% Rh/CdCO ₃ ^b	Butyric Acid	129
Crotonaldehyde	5% Rh/CaCO ₃ ^a	Butyraldehyde	59
Crotonaldehyde	5% Rh/CaCO ₃ ^b	Butyraldehyde	38
Crotonaldehyde	5% Rh/NiCO ₃ ^b	Butyraldehyde	33
Crotonaldehyde	5% Rh/CoCO ₃ ^b	Butyraldehyde	33
Crotonaldehyde	5% Rh/ZnCO ₃ ^b	Butyraldehyde	27
Crotonaldehyde	5% Rh/CdCO ₃ ^b	Butyraldehyde	23
Crotonitrile	5% Rh/CaCO ₃ ^a	n-Butyronitrile	131
Crotonitrile	5% Rh/CaCO ₃ ^b	n-Butyronitrile	34
Crotonitrile	5% Rh/NiCO ₃ ^b	n-Butyronitrile	74
Crotonitrile	5% Rh/CoCO ₃ ^b	n-Butyronitrile	47
Crotonitrile	5% Rh/ZnCO ₃ ^b	n-Butyronitrile	56
Crotonitrile	5% Rh/CdCO ₃ ^b	n-Butyronitrile	39

Table 5. Hydrogenation of Alkenes (Concluded)

Compound	Catalyst	Product	Rate x 10 ⁴ g ⁻¹ min ⁻¹
Styrene	5% Rh/CaCO ₃ ^a	Ethylbenzene ^c	175
Styrene	5% Rh/CaCO ₃ ^b	Ethylbenzene ^c	74
Styrene	5% Rh/NiCO ₃ ^b	Ethylbenzene ^c	146
Styrene	5% Rh/CoCO ₃ ^b	Ethylbenzene ^c	141
Styrene	5% Rh/ZnCO ₃ ^b	Ethylbenzene	128
Styrene	5% Rh/CdCO ₃ ^b	Ethylbenzene	62
Cinnamic Acid	5% Rh/CaCO ₃ ^a	Dihydrocinnamic Acid ^c	126
Cinnamic Acid	5% Rh/CaCO ₃ ^b	Dihydrocinnamic Acid ^c	29
Cinnamic Acid	5% Rh/NiCO ₃ ^b	Dihydrocinnamic Acid ^c	45
Cinnamic Acid	5% Rh/CoCO ₃ ^b	Dihydrocinnamic Acid ^c	41
Cinnamic Acid	5% Rh/ZnCO ₃ ^b	Dihydrocinnamic Acid	0.6
Cinnamic Acid	5% Rh/CdCO ₃ ^b	Dihydrocinnamic Acid	7.0
Methyl Cinnamate	5% Rh/CaCO ₃ ^a	Methyldihydrocinnamate ^c	105
Methyl Cinnamate	5% Rh/CaCO ₃ ^b	Methyldihydrocinnamate ^c	30
Methyl Cinnamate	5% Rh/NiCO ₃ ^b	Methyldihydrocinnamate ^c	42
Methyl Cinnamate	5% Rh/CoCO ₃ ^b	Methyldihydrocinnamate ^c	48
Methyl Cinnamate	5% Rh/ZnCO ₃ ^b	Methyldihydrocinnamate	39
Methyl Cinnamate	5% Rh/CdCO ₃ ^b	Methyldihydrocinnamate	6

a. Commercially available catalyst purchased from Engelhard Ind., Inc.

b. Catalysts prepared with NaBH₄ reduction method.

c. The aromatic ring of these compounds was later reduced.

better. The 5% Rh/ZnCO₃ catalyst was, generally, the least active especially in the case of the α,β unsaturated acids, where, rather unusually, the presence of a carboxylic acid group seemed to inhibit the activity of this catalyst to a much greater extent than any of the other catalysts studied in this research. This can be noted by comparing the very slow rate constants for the hydrogenation of cinnamic acid and crotonic acid over 5% Rh/ZnCO₃ with those rates obtained for these acids from other catalysts. Also, one should point out that the influence of the carboxylic acid group was greater on a ZnCO₃ support than on other supports as evidenced by the comparison of hydrogenation rates for cinnamic acid and methyl cinnamate for all the supports. The difference for ZnCO₃ for these two compounds is about 65 fold, where there is little or no effect shown on any of the other supports.

Hydrogenation of unhindered aliphatic α,β unsaturated aldehydes usually proceeds with the selective hydrogenation of the carbon-carbon double bond. Reduction of aromatic α,β unsaturated aldehydes to the saturated aldehyde is more difficult and the carbonyl is frequently partially reduced as well.⁽⁵¹⁾ Under certain conditions, an unhindered α,β unsaturated aldehyde such as crotonaldehyde, may be reduced to the unsaturated alcohol. Rylander and coworkers⁽⁵²⁾ were able to produce 2-butene-1-ol in high yield using platinum catalyst, supported or unsupported, with the addition of iron in the form of ferrous chloride and zinc in the form of zinc acetate. They also found that when supported platinum catalyst was used, the support was specific; carbon or calcium carbonate produced 2-butene-1-ol on hydrogenation of crotonaldehyde, whereas butyraldehyde was formed when barium sulfate or

alumina was used as support. It was necessary to have both zinc and iron present simultaneously if selective reduction of the carbonyl in crotonaldehyde was to be achieved. The presence of zinc ion in the above catalytic system was believed to inhibit carbon-carbon double bond saturation while the presence of ferrous ion promoted carbonyl reduction.

Rylander pointed out that these metals are quite specific and many futile attempts were made to replace iron and/or zinc as a promoter. Without iron present in the form of ferrous chloride, zinc promoted platinum catalyst gave only butyraldehyde. They have also tried to replace platinum with palladium, rhodium, or ruthenium, and at the same time replace ferrous chloride and zinc acetate with other metallic salts of gold, silver, tin, calcium, copper, nickel, and lead, either singly or in combination; but in every experiment, butyraldehyde was the only product.

In this research, crotonaldehyde was reduced with rhodium catalyst supported on different metal carbonates. Our results show that butyraldehyde was the only product obtained, there was no trace of 2-butene-1-ol as analyzed by gas chromatography. The presence of metal carbonates such as zinc carbonate, nickel carbonate, cobalt carbonate, or cadmium carbonate did not affect or promote the reduction of the carbonyl group. Although the system is somewhat different, it seems to agree with those results obtained by Rylander.⁽⁵²⁾ Upon complete hydrogenation with the commercial 5% Rh/CaCO₃ catalyst for 24 hours, the product distribution was 65% butyraldehyde and 35% n-butanol as shown by gas chromatography.

The reduction of aromatic α, β unsaturated aldehydes is somewhat more complicated. Several possible reduction products may result. Skita⁽⁵³⁾ found nearly pure hydrocinnamaldehyde from reduction of cinnamaldehyde with colloidal palladium by stopping the reaction after one mole equivalent of hydrogen had been absorbed. On the other hand, Tuley and Adams⁽³³⁾ have shown that when ferrous chloride and zinc acetate were added in small quantities in the hydrogenation of cinnamaldehyde with platinum oxide and the reduction stopped after one molecular equivalent of hydrogen had been absorbed, the product was almost pure cinnamyl alcohol. This agrees with the work of Rylander⁽⁵²⁾ which has just been discussed. Using palladium catalyst, Rylander and Himelstein⁽¹⁷⁾ found that the products obtained in reduction of α, β unsaturated aldehydes depended upon the solvent, substrate, support, and also upon various additives. Contrasting to the results of Tuley and Adams,⁽³³⁾ the addition of ferrous chloride in the hydrogenation of cinnamaldehyde in methanol with 5% palladium-on-carbon produced 100% hydrocinnamaldehyde. If acetic acid was used as solvent instead of methanol, the hydrogenation would proceed to give 93% phenylpropanol. Other additives were used by Rylander; hydrofluoric and hydrochloric acids were effective promoters for the reduction of cinnamaldehyde, while hydrobromic and hydroiodic acids were definitely poisons. They also showed that the support was an important factor in determining the selectivity of reduction. When alumina or calcium carbonate was used as support, the product obtained was 95-100% hydrocinnamaldehyde; however, only 50% yield of hydrocinnamaldehyde was obtained when carbon was used as support, the other 50% was phenylpropanol. They emphasized the fact

a correlation between the type of support, rate of reduction, solvent, and selectivity was not evident.

Cinnamaldehyde has also been hydrogenated with the catalysts prepared in this research. The results are shown in Table 6. The

Table 6. Hydrogenation of Cinnamaldehyde

Catalyst	Initial Rate $\text{g}^{-1} \text{min}^{-1} \times 10^4$	%HC	%CA	%Pr	% Unreacted Aldehyde
5% Rh/CaCO ₃ ^{a,c}	1.5	80.2	1.2	3.9	14.7
5% Rh/CaCO ₃ ^{b,c}	4.3	70.5	1.8	3.8	23.9
5% Rh/NiCO ₃ ^{b,c}	8.8	80.3	1.4	3.8	14.5
5% Rh/CoCO ₃ ^{b,c}	7.5	80.0	1.5	3.5	15.0
5% Rh/ZnCO ₃ ^{b,d}	4.4	41.4	8.5	-	50.0
5% Rh/CdCO ₃ ^{b,d}	5.4	40.0	6.8	-	53.2

%HC = % hydrocinnamaldehyde

%CA = % cinnamyl alcohol

%Pr = % 3-phenyl-1-propanol

a. Commercially available catalyst purchased from Engelhard Ind., Inc.

b. Catalysts prepared with NaBH₄ reduction method.

c. The reaction was stopped after the absorption of one equivalent of hydrogen.

d. The reaction stopped spontaneously after the absorption of half an equivalent of hydrogen.

hydrogenations were carried out with 0.2 moles cinnamaldehyde in 50 ml. ethanol and 2.0 gm. catalyst. The reactions were stopped after the absorption of one equivalent of hydrogen gas except in the cases of 5% Rh/ZnCO₃ and 5% Rh/CdCO₃ in which less than one equivalent of hydrogen

gas was absorbed even after prolonged reaction time. The reaction mixtures were analyzed with vapor phase chromatography against standard known samples. The percentage distribution of products was determined by the ratio of the different peak areas corrected with known quantities of standard samples. As indicated in the results, a small amount of unsaturated alcohol was obtained. The amount was relatively negligible in the first four cases on Table 6 in comparison to the amount of hydrocinnamaldehyde obtained. However, in the cases when either zinc or cadmium carbonates was used as support, the relative amount of cinnamyl alcohol increased. As previously stated, the addition of zinc ion was effective in producing unsaturated alcohol. It may be speculated that the zinc carbonate performs the same function as the zinc ion added in platinum oxide catalyst. A more realistic reason may be that the reduction of olefin with these two catalysts proceeded at such a slow pace that the reduction of the carbonyl group, though also slow, was observed to be occurring simultaneously; that is, the rates of hydrogenation of each function were more nearly the same.

Olefins are hydrogenated rapidly and readily in the presence of a nitrile group. Such was the case when crotononitrile was reduced with the catalysts prepared. In every instance, n-butyronitrile was the only product formed after the absorption of one equivalent of hydrogen gas. Upon further hydrogenation, the nitrile function was also reduced but at a much slower rate indicated by the slow absorption of hydrogen. It is commonly known⁽⁵⁴⁾ that primary, secondary, or tertiary amines may be obtained when nitrile functions are hydrogenated. However, no

evidence of secondary or tertiary amine was shown in the v.p.c. analysis in this work, n-butylamine was the only peak shown besides that of the starting material.

Reduction of the Nitro Group

In general, aromatic nitro compounds can be reduced at room temperature and under slight hydrogen pressure with rhodium, palladium, or platinum on various supports. Although the reduction is believed to be a stepwise process, yet there is no record of partial catalytic reduction of nitrobenzene to nitrosobenzene or other nitrogen grouping. The isolation of phenylhydroxylamine during hydrogenation of nitrobenzene is not always possible after the uptake of two equivalents of hydrogen gas.⁽⁵⁵⁾ It was suggested that the exothermicity of the reduction of aromatic nitro group supplies enough energy to aid rapid reduction of the intermediates to the amine as well.⁽⁵⁶⁾ It may also be due to the fact that the intermediates are reduced at least as rapidly as nitrobenzene is since no change in rate is observed.

As a rule, methyl and ethyl alcohols are excellent solvents for reduction of nitrobenzene. Acetic acid is also useful, since it is believed that the presence of acid will decrease the inhibitory effect of the amino nitrogen and therefore should prevent the deactivation or poisoning effects the basic amine has upon these catalysts. Unfortunately, the use of acetic acid or any strong acid as solvent is not appropriate in this research, since the acid will effect some decomposition of the carbonate supports and thus alter the nature of the catalysts.

Yao and Emmett⁽⁵⁷⁾ have found that in the reduction of a series

of p-substituted nitrobenzenes to the amines with colloidal rhodium catalyst, the reaction rates were affected by the electronic effects of the substituents and by the presence of acid or base. They noticed that substituents on nitrobenzene can affect the reaction only when the reaction is first order or fractional order with respect to the nitro compound. In essence, the reduction under these conditions was diffusion controlled.

Nitrobenzene was hydrogenated with the catalysts prepared in this research and the results are shown in Table 7.

Table 7. Hydrogenation of Nitrobenzene

Catalyst	Rate $\text{g}^{-1} \text{min}^{-1} \times 10^4$	Product
5% Rh/CaCO ₃ ^a	13.5	Aniline ^c
5% Rh/CaCO ₃ ^b	8.5	Aniline ^c
5% Rh/NiCO ₃ ^b	5.0	Aniline ^c
5% Rh/CoCO ₃ ^b	4.0	Aniline ^c
5% Rh/ZnCO ₃ ^b	1.0	Aniline
5% Rh/CdCO ₃ ^b	11.0	Aniline

a. Commercially available catalyst purchased from Engelhard Ind., Inc.

b. Catalysts prepared with NaBH₄ reduction method.

c. Aromatic ring could later be reduced.

When CaCO₃, NiCO₃, or CoCO₃ was used as support in the reduction of nitrobenzene, the product obtained at the end of the reaction was cyclohexylamine. However, if the reaction was stopped after 3 equivalents of hydrogen gas was absorbed, a good yield of up to 90% of aniline

was obtained. In the case of zinc carbonate, the reduction stopped after 3 equivalents of hydrogen was absorbed, and aniline was the only product obtained. Cadmium carbonate supported catalyst seemed to be exceptionally useful in the reduction of the nitro group as evidenced by its comparatively rapid rate. After 19 hours and about 3 1/2 equivalent of hydrogen was absorbed, the yield was 90% aniline and 10% cyclohexylamine.

Aromatic Ring Systems

The carbocyclic aromatic nucleus may be hydrogenated readily over platinum metal catalysts. Platinum, usually as platinum oxide, and rhodium are used frequently under mild conditions, whereas ruthenium and palladium catalysts are used mostly at elevated temperatures and pressures.

In general, acidic conditions are necessary for ring reduction when a platinum catalyst is employed. Acidic conditions also can lead to an increase in hydrogen uptake in palladium-catalyzed reactions, but is usually unnecessary in those employing rhodium catalysts. In fact, it has been shown that the addition of hydrochloric acid had an adverse effect on the reduction of toluene or benzoic acid in methanol with 5% rhodium-on-carbon. On the other hand, the addition of weaker acids to the same hydrogenation had neither a retarding nor an enhancing effect. Stocker⁽²¹⁾ later found that small amounts of acetic acid strongly promoted hydrogenation of certain aromatics over rhodium-on-alumina in methanol. Once again it may be pointed out that the use of acidic solvent or the addition of acid is not appropriate in the cases

of carbonate supported catalysts because the carbonate may be decomposed.

Benzene and benzoic acid were hydrogenated in ethanol with the catalysts prepared and the results shown in Table 8.

Table 8. Hydrogenation of Aromatic Ring System

Compound	Catalyst	Product	Rate, $k \times 10^4 \text{ g}^{-1} \text{ min}^{-1}$
Benzene	5% Rh/CaCO ₃ ^a	Cyclohexane	59
Benzene	5% Rh/CaCO ₃ ^b	Cyclohexane	4.8
Benzene	5% Rh/NiCO ₃ ^b	Cyclohexane	12.4
Benzene	5% Rh/CoCO ₃ ^b	Cyclohexane	4.9
Benzene	5% Rh/ZnCO ₃ ^b	No Reaction	--
Benzene	5% Rh/CdCO ₃ ^b	Cyclohexane	3.1
Benzoic Acid	5% Rh/CaCO ₃ ^a	Cyclohexylcarboxylic Acid	18.5
Benzoic Acid	5% Rh/CaCO ₃ ^b	Cyclohexylcarboxylic Acid	c
Benzoic Acid	5% Rh/NiCO ₃ ^b	Cyclohexylcarboxylic Acid	1.4
Benzoic Acid	5% Rh/CoCO ₃ ^b	Cyclohexylcarboxylic Acid	c
Benzoic Acid	5% Rh/ZnCO ₃ ^b	No Reaction	--
Benzoic Acid	5% Rh/CdCO ₃ ^b	No Reaction	--

a. Commercially available catalyst purchased from Engelhard Ind., Inc.

b. Catalysts prepared with NaBH₄ reduction method.

c. The rate was too slow to be calculated.

The results show that benzene was reduced readily over 5% Rh/CaCO₃, 5% Rh/NiCO₃, 5% Rh/CoCO₃, and 5% Rh/CdCO₃, but at a much slower rate in comparison to the other functional groups. Although it has been suggested that hydrogenation of a benzene ring proceeds in stages,⁽⁵⁸⁾ i.e. via cyclohexadiene and cyclohexene, yet no evidence of the dihydro or tetrahydro benzenes were observed in the v.p.c. analysis. There were no sudden changes in the rate of absorption of hydrogen throughout the reaction. Thus one may conclude either a one-step process is involved or the rate controlling step is the formation of products, which in turn are hydrogenated to the saturated compound at a more rapid rate. Evidence of this latter conclusion comes from the observed rate constants for cyclohexene hydrogenation (Table 4) which are roughly 3-40 times faster than those for benzene.

The hydrogenation of benzoic acid did not occur readily except over the commercial catalyst. Usually, the ease of reduction of the aromatic ring system is dependent on substituents and their number. Compared with benzene the presence of a substituent on the ring increases the difficulty of reduction, except when the substituent is a phenolic hydroxyl group. The presence of a carboxyl group, either as acid or ester, usually has a definite retarding effect on hydrogen uptake. It is not surprising, therefore, to find that the catalysts prepared in this work were much less active in the hydrogenation of benzoic acid.

In the hydrogenation of styrene, the carbon-carbon double bond of the olefinic linkage was reduced readily with the absorption of one equivalent of hydrogen gas. When 5% Rh/CaCO₃, 5% Rh/NiCO₃, or 5% Rh/CoCO₃ was used as catalyst. The reduction continued though at a

much slower rate until the aromatic ring was saturated. The initial absorption of hydrogen beyond one equivalent was still a linear function of time. From this, the rate of the ring hydrogenation was calculated and is tabulated in Table 9.

Table 9. Hydrogenation of Aromatic Ring of Styrene

Catalyst	Rate, $k \times 10^4 \text{ g}^{-1} \text{ min}^{-1}$	Product
5% Rh/CaCO ₃ ^a	3.8	Ethylcyclohexane
5% Rh/CaCO ₃ ^b	0.9	Ethylcyclohexane
5% Rh/NiCO ₃ ^b	1.9	Ethylcyclohexane
5% Rh/CoCO ₃ ^b	2.7	Ethylcyclohexane
5% Rh/ZnCO ₃ ^b	No Reaction	--
5% Rh/CdCO ₃ ^b	No Reaction	--

a. Commercially available catalyst purchased from Engelhard Ind., Inc.

b. Prepared with NaBH₄ reduction method.

As was pointed out in Chapter 1, rhodium catalyst, in its various catalytic forms, is particularly useful for its ability to foster hydrogenation of aromatic systems at low pressure and often in the absence of acidic media. The carbonate supported catalysts, on the other hand, were found to be more active in the reduction of olefinic linkages and nitro groups than in the reduction of aromatic ring system. Zinc carbonate supported catalyst in particular is completely inactive towards the hydrogenation of the ring system. It is suggested, therefore, that this catalyst would be quite useful in selective hydrogenation of

certain functional groups in the presence of aromatic rings.

Copper Carbonate Support

The use of copper carbonate as support for rhodium catalyst was also studied. The catalyst was prepared in a similar manner by the three different methods. Both the catalysts prepared with formaldehyde reduction and hydrogen gas reduction were found to be ineffective when used in the hydrogenation of cyclohexene; whereas that prepared with NaBH_4 reduction method yielded a rate constant of $102 \text{ g}^{-1} \text{ min}^{-1} \times 10^{-4}$ for the same reduction. The same catalyst effected the hydrogenation of crotononitrile with a rate constant of $35 \text{ g}^{-1} \text{ min}^{-1} \times 10^{-4}$ and was ineffective when used in the hydrogenation of benzoic acid. In general, this catalyst was less active than any of the previous ones. The most interesting result occurred when 5% Rh/CuCO_3 was used in the hydrogenation of crotonaldehyde. Upon analysis of the product with v.p.c., an unknown compound showed up which constituted about 50% of the product mixture. The compound when isolated and analyzed yielded a compound of the molecular formula of $\text{C}_8\text{H}_{10}\text{O}_2$ which is exactly double that of n-butylaldehyde. The identity of the compound has yet to be determined. During this hydrogenation reaction, the copper carbonate itself was also being reduced to metallic copper, a shiny metallic surface appeared on the side of the hydrogenation bottle. The ethanol solvent became bluish green in color. It has been known that metallic copper is a good catalyst for several types of reaction; it is quite possible that during the hydrogenation reaction, this metallic copper, formed from the reduction of copper carbonate, catalyzed a reaction between two molecules

of n-butyraldehyde. It is also possible that the copper ions form a complex with the substrate which is soluble in ethanol, thus contributing to the greenish color. The same catalyst was also used for the hydrogenation of cinnamaldehyde with similar interesting result. A compound which constituted about 50% of the product mixture showed up on v.p.c. which did not correspond to any of the expected products. The identity of this compound has yet to be determined.

Effect of Geometrical Configuration

There appears to be a general opinion that cis double bond isomers are hydrogenated more rapidly than the corresponding trans isomers. To investigate this, the relative rate of hydrogenation of the cis and trans isomers of crotonic acid were studied by Plisov and Bogatsky.⁽⁵⁹⁾ They found that the cis isomer was hydrogenated more rapidly with palladium-on-barium sulfate in ethanol. Other workers who studied the reduction of a series of cis and trans unsaturated acids gave similar results.⁽⁶⁰⁾ In the present work, the hydrogenation of maleic acid (cis) and fumaric acid (trans) was studied with each of the catalysts prepared. Table 10 shows the results of this work. In each instance, the expected reduction product of succinic acid was obtained.

It is quite evident with each catalyst that the cis isomer was reduced more rapidly than the trans isomer. Since the addition of hydrogen to an olefinic linkage proceeds in a cis manner in catalytic hydrogenation reactions, it is not surprising that the stereo structure of the trans isomer (fumaric acid) hinders the approach of the hydrogen, whereas, hydrogen approaching a cis molecule (Maleic acid) is

sterically hindered only on one "side" of the adsorbed molecule leaving the other "side" quite available for reaction.

Table 10. Hydrogenation of Maleic and Fumaric Acids

Catalyst	Maleic Acid Rate, $\text{g}^{-1} \text{min}^{-1} \times 10^4$	Fumaric Acid Rate, $\text{g}^{-1} \text{min}^{-1} \times 10^4$
5% Rh/CaCO ₃ ^a	267	173
5% Rh/CaCO ₃ ^b	134	91
5% Rh/NiCO ₃ ^b	221	188
5% Rh/CoCO ₃ ^b	192	169
5% Rh/ZnCO ₃ ^b	59	26

a. Commercially available catalyst purchased from Engelhard Ind., Inc.

b. Catalysts prepared with NaBH₄ reduction method.

Surface Area

As indicated in the first chapter of this thesis, surface area of the catalyst is one of the factors which may influence the activity of that catalyst. Maxted and coworker⁽¹⁰⁾ had attempted to establish a relationship between the activity and surface area in a series of platinum catalysts on various oxide supports; however, they reported that no meaningful correlation was found. Poltorak⁽⁶¹⁾ has studied the hydrogenation of 1-hexene and of cyclohexene in liquid phase on Pt/silica catalysts and concluded the reactions took place at the active centers of the catalyst and that the structure of the surface and the difference between crystal faces and crystal edges seemed to have no effect on the

formation of these active sites. Poltorak also indicated that the role of structural effects in hydrogenation catalysis on platinum has been greatly over-emphasized.

Dorling and Moss⁽⁶²⁾ have also carried out studies on the Pt/silica system. They found a constant specific activity for the gas phase hydrogenation of benzene at 25°C despite a wide variation in the crystallite size of the catalysts. They concluded that the activity for the reaction was not sensitive to the state of dispersion of the catalyst.

Boudart et al.⁽⁶³⁾ studied the hydrogenolysis of cyclopropane on platinum at 0°C. The specific activity of the metal was found to be independent of platinum content on two different forms of alumina, and independent of the nature of the support whether alumina or silica gel, and only a two-fold change in activity was noticed between the highly dispersed samples and the rest, while the surface area varied by more than four orders of magnitude. Thus, in a single study, the absence of metal-support interaction and the lack of sensitivity to surface structure were demonstrated.

We have measured the surface areas of the carbonate supported catalysts by the B.E.T. method employing nitrogen at liquid nitrogen temperatures. The results are given in Table 11.

The results indicate that the 5% Rh/CaCO₃ prepared with NaBH₄ reduction method has a somewhat smaller surface area than that of the commercial sample. The other catalysts have considerably smaller surface areas than the commercial 5% Rh/CaCO₃. The activities of these catalysts as shown in an earlier part of this chapter, however, have no direct correlation with these surface areas. The 5% Rh/NiCO₃ and

5% Rh/CoCO₃ for example, though having a much smaller surface area than 5% Rh/CaCO₃, yet were found to be more active in the hydrogenation of most of the compounds studied in this research than when 5% Rh/CaCO₃ was used. One can, therefore, conclude that the activity of the catalysts are independent of the surface area of the catalysts, but is dependent upon the active sites of the surface. The hydrogenations are, therefore, structure insensitive.

Table 11. Surface Area of Catalyst

Catalysts	Surface Area Sq. m./gm
5% Rh/CaCO ₃ ^a	7.5
5% Rh/CaCO ₃ ^b	5.8
5% Rh/NiCO ₃ ^b	0.26
5% Rh/CoCO ₃ ^b	0.58
5% Rh/ZnCO ₃ ^b	0.23

CHAPTER IV

CONCLUSIONS

A series of rhodium catalysts was prepared using different carbonates and these were used in the hydrogenation of various functional groups in organic compounds.

Of the three different methods used in the preparation of the catalysts, namely, formaldehyde reduction, hydrogen gas reductions, and sodium borohydride, the last method was found to be the most effective.

Upon plotting $\log P_o/P_t$ versus time for each of the reactions, the straight line, characteristic of first order kinetics, was obtained. From the slope of this line, a rate constant of each hydrogenation reaction was calculated.

In almost all instances, the commercially purchased 5% Rh/CaCO₃ catalyst was more effective than any of those prepared in this work.

All the catalysts were found to be efficient in the hydrogenation of olefinic double bonds. Five percent Rh/NiCO₃ and 5% Rh/CoCO₃ were more effective than the other catalysts. When 5% Rh/ZnCO₃ was used in the hydrogenation of olefinic double bond, the activity was sharply decreased if there was a carboxylic acid group adjacent to the double bond.

When used in the hydrogenation of nitro group, all the catalysts were only moderately effective except 5% Rh/CdCO₃ which showed exceptional efficiency in the reduction of nitro group.

The aromatic ring could be hydrogenated by using all the catalysts prepared in this research except 5% Rh/ZnCO₃. The rate was much slower than that for an olefinic double bond and in the case of benzoic acid, the hydrogenation was so slow that it became impractical to use them as catalysts. Five percent Rh/ZnCO₃, on the other hand, may be useful in hydrogenation of other functional groups in the presence of aromatic rings.

All the catalysts were found to be inactive towards the hydrogenation of carbonyl function. Only in one case in which the catalyst used was commercial 5% Rh/CaCO₃ and the reaction was carried out a prolonged length of time was hydrogenation of a carbonyl noted. Thus, a selective hydrogenation of carbon-carbon double bond was able to be obtained by controlling the amount of hydrogen absorbed.

The role played by the carbonate supports in these hydrogenation reaction with rhodium catalysts was not entirely clear. In general, the catalysts behaved "normally" and reduced the more readily reducible function group as expected. Surface areas of these catalysts were found to have no apparent direct relationship with the activity of these catalysts.

CHAPTER V

RECOMMENDATIONS

This work is a survey of the effectiveness of carbonate supports when used in hydrogenation reactions. In order to understand the role of these supports in hydrogenation reactions, a more extensive list of compounds should be studied using these catalysts. It should at least include ketones, α,β unsaturated ketones, heterocyclic aromatic compounds and also acetylenic compounds.

The use of copper carbonate as support should be studied in greater detail, especially when it is used in the hydrogenation of α,β unsaturated aldehydes.

Ferrous ion as was pointed out in Chapter 1, promotes the reduction of carbonyl groups. Since all the catalysts prepared in this research were ineffective towards the hydrogenation of aldehydes, it will be interesting to study the effect of ferrous carbonate as a support.

The use of other platinum metals such as platinum, palladium, etc., as catalyst will provide further knowledge of the effect of carbonate supports.

Ultimately, the use of nickel oxide, cobalt oxide, zinc oxide, etc., should be used as supports in order to find out if the metal ions indeed have modifying effect on the catalysts.

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