

Hydrogenation of Natural Oils With Platinum Metal Group Catalysts

PAUL N. RYLANDER, Engelhard Industries, Newark, N.J. 07105

Abstract

Studies in the hydrogenation of natural oils with catalysts of the platinum metals group have been limited mainly to platinum and palladium with only scant attention to rhodium, ruthenium, iridium and osmium. This preference was dictated largely by economics, palladium being the only noble metal catalyst truly competitive on a use-coat basis with nickel in the hydrogenation of low-priced oils. This paper discusses the noble metal catalysts as a group, points out similarities and differences among the metals relevant to the hydrogenation of natural oils, and describes some of the practical applications of catalysis by palladium.

General Characteristics of Noble Metal Catalysts

Characteristics of catalysts relevant to the hydrogenation of natural oils, which is essentially the chemistry of olefin hydrogenation, are activity for saturation, selectivity for removal of multiple unsaturation, relative tendencies to promote *cis-trans* isomerization, double bond migration, 1,4 addition and, in certain compounds, hydrogenolysis. A factor extrinsic to the catalyst itself is the role hydrogen diffusion to the catalyst surface plays in the determination of these characteristics. The extreme activity of certain noble metal catalysts frequently causes the rate determining step to be one of mass transport. This phenomenon, well-known with nickel, is greatly accentuated in the more active platinum metal catalysts.

Activity

Activity sequences are the most nebulous of catalyst characteristics for the absolute and perhaps even relative activity depend on the support, method of preparation, substrate, impurities and reaction conditions. Nonetheless, a general sequence for activity for olefin saturation can be written, which is $\text{Pd} > \text{Rh} > \text{Pt} \gg \text{Ir} > \text{Ru} \gg \text{Os}$.

The demarcation between the first three and last three catalysts is sharp, rendering the latter catalysts uneconomical for production of low cost products derived by olefin hydrogenation. The first three catalysts are exceedingly active and their ordering is of little consequence because diffusion controls the reaction rate. Data illustrating how easily hydrogenation over one of these very active catalyst may become diffusion controlled is given in Table I. The catalyst functioning rate, expressed as iodine units reduction per minute per 1% of catalytic metal increases steadily as the percentage of palladium based on oil is decreased. At the lowest concentrations the rate is not yet proportional to the amount of metal present. Over the range of metal concentration studied the catalyst functioning rate varied by a factor of 20 (1). By inspection of the data a completely erroneous view of the economics of using palladium will be obtained if superfluous catalyst is used. At very low metal

loadings the catalyst is sensitive to poisons and again a low estimate of catalyst efficiency might be obtained. Under conditions where an appreciable percentage of the catalyst is poisoned, an incremental addition of catalyst may bring about large percentage increases in rate. It is usually difficult to get a fair evaluation of catalyst efficiency from only one catalyst loading level.

Double Bond Migration

The rate ratio of double bond migration to hydrogenation has a profound effect on the composition of products derived by partial hydrogenation of olefins. Many authors have noted a parallelism between *cis-trans* isomerization and selectivity. Each reaction separately has been linked to the variables pressure, temperature, agitation, catalyst concentration and solvent through the effect these factors have on hydrogen availability at the surface (1,2). Coenen (3) noting that these variables also influenced double bond migration in an identical direction (4), proposed a causal relationship among them, with migration into conjugation being a requisite for high selectivity. Supporting evidence, in terms of accumulation of intermediate conjugated diolefins was lacking however, due undoubtedly to the operation of a hierarchy of decreasing adsorbabilities: conjugated dienes, non-conjugated dienes, monoenes. Even in partial hydrogenation of monoenes the composition of the product is determined by the tendency of the catalyst to promote migration.

The rate ratio of double bond migration to hydrogenation is a property of the catalytic metal. Table II made from studies of low molecular weight olefins shows how widely noble metals differ in their tendency to promote migration as well as how this relative tendency varies with the olefin structure. The authors recorded the order for double bond migration $\text{Pd} > \text{Ni} > \text{Rh} \sim \text{Ru} > \text{Os}$, Ir , Pt and noted it is the same order as the ability of the metals to dissolve hydrogen (5). The same ordering of these metals has been adduced from a large number of experiments on small olefins and the observation made that ordering is unchanged by support or solvent (6). Rhodium is unique among the metals in that the rate of isomerization relative to the rate of hydrogenation is markedly changed by temperature. At low temperature the relative rate of isomerization is small and rhodium resembles platinum, whereas at higher temperature (above 80 C) the relative rate of isomerization is much larger and resembles palladium; the effect is due to increasing probability of olefin desorption (7).

TABLE I

Effect of Catalyst Concentration on Rate ^a	
% Palladium in oil	Catalyst functioning rate
0.02	18
0.1	40
0.005	72
0.0025	130
0.00125	215
0.0005	354

¹One of 10 papers to be published from the Symposium "Hydrogenation," presented at the AOCs Meeting, New Orleans, April 1970.

^aCatalyst 0.5% palladium-on-carbon; temperature, 185 C; pressure, atmospheric; agitation, 620 rpm; 70% soybean, 30% cottonseed oil.

TABLE II
Effect of Metal on Selectivity Coefficient

Metal	Selectivity coefficient ^a			
	1-Hexene	2-Methyl-1-pentene	3-Methyl-1-pentene	2,3-Dimethyl-1-butene
Ni	1.45	0.69	0.25	0.13
Ru	0.41	0.63	0.06	0.11
Rh	0.49	1.1	0.06	0.13
Pd	1.7	12.7	1.1	5.3
Os	0.19	0.09
Ir	0.1	0.1
Pt	0.12	0.13

^a Selectivity coefficient of isomerization = % isomerization/% hydrogenation; 40 C ethanol solvent.

The relative rate of isomerization is influenced also by factors extrinsic to the catalytic metal as exemplified by a study of migration during hydrogenation of optically active (-)-3,7-dimethyl-1-octene. Racemization, and by inference isomerization, decreased with increasing pressure over palladium-on-carbon, the product being for 1, 2 and 100 atmospheres, 52%, 37% and 23% racemized. Migration also decreased as the amount of catalyst decreased, falling from 52% to 43% to 32% as the catalyst was decreased from 0.05 g to 0.01 g to 0.003 g. Both of these effects may be related to hydrogen availability at the catalyst surface and tend in the direction of hydrogen-rich catalysts diminishing migration. The authors suggested, on the other hand, that since various inhibitors also diminish migration the effect may have arisen by the smaller amounts of catalysts being inhibited inadvertently (8).

Various additives also had a marked effect on diminishing migration. The presence of small amounts of potassium hydroxide or pyridine reduced migration from 52% to 12% and 18%, respectively. The authors suggested that the inhibitors block certain sites with enhanced activity for migration. There is probably also a contribution from the effect of hydrogen availability at the catalyst surface since the rate of hydrogenation was sharply decreased by the presence of these additives.

The variables of pressure, concentration and additives would be expected to operate in the same direction with the other noble metals but with less effect since their tendency to isomerization is much less than palladium's. For example, in the above hydrogenation where palladium-on-carbon gave 52% migration, platinum oxide gave only 3%. (Platinum oxide in acetic acid is in fact a generally recommended catalyst system when migration is to be avoided.) Migration over nickel in hydrogenation of methyl oleate increased with increasing temperature, catalyst concentration, and decreasing agitation; under comparable conditions palladium gave more positional isomers than nickel (9).

Cis-Trans Isomerization

Olefins in the presence of noble metal catalysts can undergo *cis-trans* isomerization; the process is tremendously speeded if carried out in the presence of hydrogen. Two types of isomerization may be distinguished. Isomerization may occur without a shift in the position of the double bond or it may occur as a consequence of migration. These processes are frequently pictured as proceeding through a common intermediate, an adsorbed alkyl radical, but the evidence demanding a common intermediate is not compelling. In experiments using platinum group metal catalysts for hydrogenation of natural oils these processes have for the most part not been distinguished

TABLE III
Hydrogenation of Tall Oil Fatty Acids Effect of Metal on *Trans* Content^a

Catalyst	% Metal in oil	% <i>Trans</i>	Catalyst functioning rate
5% Rh/C	0.05	26.0	39.6
5% Ru/C	1.00	13.2	1.0
5% Ir/C	0.50	9.7	2.4
5% Pt/C	0.05	6.0	5.8
5% Pd/C	0.025	30.6	72.8
1% Pd/C	0.025	27.8	80.4
1% Pd/C ^b	0.100	24.8	7.2

^a Solvent: methanol; 1 atm.; 28 C; Pd > Rh > Ru > Ir > Pt.

^b Modified by silver and bismuth.

and the comparison usually made is of total isomerizing activity.

In hydrogenation of tall oil fatty acids over the noble metal catalysts Zajcew (10) formulated the order of increasing tendency to *trans* formation Pt < Ir < Ru < Rh < Pd (Table III). This is the same order given above for activity in double bond migration, and one may infer a relationship between the two reactions. At the expense of activity, *trans* isomer formation may be decreased by partial deactivation of the catalyst an effect paralleled in decreasing migration of the double bond. Table III also illustrates that more efficient use is made of the metal as the concentration on the carrier is decreased.

The *trans* isomer content, obtained at hydrogenation to substantially the same iodine number, correlated in one sense with the catalyst functioning rate; those catalysts (Rh and Pd) with very high rates produced large amounts of *trans* isomer, whereas those with low rates (Ru, Ir and Pt) produced much less. Riesz and Weber (11) established the order for increasing *trans* isomer formation in hydrogenation of soybean oil as Pt < Rh < Pd. *Trans* isomer formation increased somewhat with metal concentration on the carrier. With palladium the use of barium sulfate as a carrier suppressed *trans* isomer formation without appreciably affecting activity or selectivity. The ordering of catalysts for *cis-trans* isomerization activity is not invariant and may change with special substrates (12), but it seems clear, that rhodium and palladium are preferred catalysts when isomerization is to be maximized; ruthenium, iridium and platinum are preferred when isomerization is to be minimized.

Effect of Hydrogen Availability

Cis-trans isomerization activity has been shown to be related to process variables in a way that can be correlated with hydrogen availability at the catalyst surface. The correlation derived from experimental data, but also reasonable on theoretical grounds, is based on the assumption that isomerization has a lower order dependency on hydrogen concentration than does hydrogenation, hence the greater the deficiency of hydrogen at the catalyst surface, the more hydrogenation will be retarded relative to isomerization.

Two measures of the effect of hydrogen availability are the effect of pressure and of agitation. Table IV illustrates the effect of pressure over the range 0 to

TABLE IV
Hydrogenation of Tall Oil Fatty Acids Effect of Pressure on *Trans* Content^a

Catalyst	Pressure psig	% <i>Trans</i>
5% Pd-on-C	0	42
5% Pd-on-C	500	28
5% Pd-on-C	1900	22

^a Solvent: methanol; temperature: 24-28 C.

1,900 psig on the percentage of *trans* isomers formed in partial hydrogenation of tall oil fatty acids in methanol at 24–28 C. Adequate data are lacking to illustrate the effect of pressure with other noble metal catalysts, but one may anticipate that except for rhodium the changes induced by pressure would be much less, for the other catalysts have both a lower functioning rate and a lower innate tendency to promote isomerization.

The effect of agitation on *trans* isomer content may be illustrated by the work of Zajcew (1) on the hydrogenation of mixtures of cottonseed and soybean oil over 5% palladium-on-carbon to produce shortening stocks. At constant conditions of 115 C, 42 psig, and a catalyst loading of 0.005% palladium based on oil, the maximum percentages of *trans* isomers varied from 37% at a stirring rate of 800 rpm to 53% when the rate was decreased to 290 rpm.

Mixed Metal Catalysts

A recent promising development in platinum metal catalysts used for fat hydrogenation is derived from the synergistic effects of two metals. *Trans* isomers have been decreased and improved rates have been obtained by discriminate use of two metals together. For example, incorporation of less than 3% platinum or 5% rhodium based on palladium in a 0.5% palladium-on-alumina catalyst caused an increase in the rate of cottonseed oil hydrogenation but a decrease in the *trans* isomers. The total amount of saturated material was increased slightly. Larger amounts of the complementary metal have an adverse effect. The tests were made under nondiffusion controlled conditions where the rate was proportional to the amount of catalyst (13). In another example hydrogenation of cottonseed oil in ethanol at 60 C over 1% palladium-on-carbon produced a product with 37.4% *trans* isomer, whereas a 1% palladium-0.01% platinum-on-carbon catalyst afforded a product with only 17% *trans* isomers at the same hydrogen absorption. Further decreases were achieved at higher platinum levels (14). Synergistic effects in hydrogenation of cottonseed oil have been shown also by palladium catalyst containing equal amounts of ruthenium, a surprising finding because of the low activity for ruthenium in olefin hydrogenation.

The changes induced by the incorporation of small amounts of other noble metals holds promise for further development. Most previous attempts to modify catalysts by the incorporation of elements not in the platinum metal group have resulted in catalysts of sharply decreased activity. In other fields where the use of mixed noble metal catalysts has been explored more extensively, striking changes in both rate and selectivity have been recorded (15,16), but as yet no extensive work on the effect of these catalyst on rate, *cis,trans* isomerization, or selectivity in olefin hydrogenation has been done.

Mode of Hydrogen Addition

Allen (17), after examining the hydrogenation of methyl *cis*-10, *cis*-12-octadecadienoate over nickel, concluded that hydrogen had added equally by 1,2, 1,4 and 3,4 addition, and further, that because of a strongly preferred orientation of the adsorbed molecule, the bond at 11 formed through 1,4 addition was *trans* (17). In conjugated dienes derived by migration, the same sort of considerations apply, and both the position of the bond remaining after addition of hydrogen and its configuration will depend on the

relative amounts of 1,2, 3,4 and 1,4 addition (18). Apparently no studies have been made with fats that will permit an assignment of the relative tendencies of noble metals to promote 1,4 addition, but the findings from studies of hydrogenation of butadiene are revelant. *Trans*-2-butene may arise from butadiene by 1,4 addition or by 1,2 addition followed by migration. Butadiene exists in the gas phase almost entirely as the antic conformer and presumably this is the major conformer in the adsorbed state as well. Addition of hydrogen in the 1,4 mode will produce *trans*-2-butene predominately whereas 1,2 addition of hydrogen followed by migration will produce the same ratio of *trans*-isomer as is found in butene-1 isomerization.

The excess ratio of *trans*-isomer to *cis* isomer obtained from butadiene hydrogenation over that obtained from butene-1 isomerization thus becomes a measure of the amount of 1,4 addition. By this criterion palladium and cobalt alone exhibit a marked tendency to 1,4 addition, whereas iron, nickel, copper, ruthenium, rhodium, osmium, iridium and platinum tend to hydrogenate predominately by 1,2 addition. The *trans-cis* ratios obtained by hydrogenation of butadiene over cobalt and palladium exceed thermodynamic equilibrium values whereas the other metals afford less than equilibrium values (19).

Steric hinderance near the double bond may alter the amount of 1,4 addition. For instance, butadiene over platinum gave little or no 1,4 addition, whereas 2,3-dimethyl-2-butene is obtained, presumably by 1,4 addition, from 2,3-dimethyl-1,3-butadiene in about 30% yield (20). Although the ease of 1,4 addition may change with the structure it seems likely that the relative order of the metals in promoting this reaction will remain the same with palladium favored when 1,4 addition is desired and avoided when it is not.

Selectivity

Most investigators seem to agree there is a causal relationship between selectivity and double bond migration and that the obtainment of high selectivity in hydrogenation of initially nonconjugated dienes depends upon a prior isomerization into conjugation (21). Migration of nonconjugated double bonds into conjugation is probably a necessary but not sufficient condition for high selectivity; a selective catalyst must in addition to an isomerizing ability have the ability to hydrogenate selectively conjugated systems. The establishment of a hierarchy of increasing selectivity over noble metal catalysts is relevant, therefore, to the problem of selective hydrogenation of nonconjugated systems. There seems to be also general agreement that selectivity is influenced by reaction variables in a way that is related to the effect of these variables on hydrogen availability at the catalyst surface; hydrogen-rich catalysts tend toward lower selectivity, hydrogen-poor catalysts toward higher selectivity. These relationships have been established for only a few metals, but presumably they should hold for all in varying degrees.

Catalysts

A number of workers have noted high selectivity in hydrogenation of natural oils over palladium or rhodium, and low or random selectivity for platinum (22). However, in hydrogenation of soybean oil over platinum-on-carbon, alumina or silica selectivity was described as good, an effect attributed to the use of elevated temperatures (11). Zajcew (10) compared selectivities of five noble metals in hydrogenation of

TABLE V
Selectivity of Hydrogenation of Tall Oil Fatty Acids

Catalyst	% Metal in oil	% Linoleic acid	% Saturated acid	% Oleic acid
5% Pd-on-C	0.025	11.6	8.8	79.6
5% Rh-on-C	0.05	16.5	14.0	69.5
5% Pt-on-C	0.05	19.9	15.3	64.8
5% Ru-on-C	1.0	20.0	17.2	62.8
5% Ir-on-C	0.5	21.6	23.6	54.8

tall oil fatty acids with the results shown in Table V. He adduced the sequence for increasing selectivity: Ir << Ru < Pt < Rh < Pd. The sequence may be compared to the slightly different order of increasing selectivities adduced for the conjugated molecules butadiene and 1,3-pentadiene (23) Ir << Pt ~ Rh < Ru < Pd. Presumably the order will hold for conjugated dienes generally.

Oleate Shunt

Selectivity in hydrogenation of multiple unsaturation involves both a mechanistic and thermodynamic factor. The mechanistic factor refers to absorption of more than 1 mole of hydrogen in a single residence of the substrate on the catalyst surface and the thermodynamic factor to competition of the more and the less unsaturated substrates for catalyst sites. Dutton (24) using radioactive tracers demonstrated the existence of a large mechanistic factor, the so-called oleate shunt, in hydrogenation of methyl linolenate over nickel catalysts, where 29% of the linolenate was reduced directly to the monoene stage without intervention of a desorbed diene. No similar measurements appear to have been made on fatty oils with noble metal catalysts, but one might infer from small molecules that palladium is preferred when addition of only one molecule of hydrogen is desired, whereas iridium and osmium are preferred when intermediate stages of hydrogenation are to be by-passed.

Metal Concentration

Selectivity is altered somewhat by the concentration of metal on the carrier, increasing generally with decreasing metal concentration. Riesz and Weber (11) suggested the use of 0.5% concentrations or even lower to obtain maximum selectivity in hydrogenation of soybean oil. Selectivity was greater over 0.5% palladium-on-carbon than over 5.0% in hydrogenation of cottonseed oil to shortening stock (1) and 1.0% palladium-on-carbon was more selective than 5% in hydrogenations for margarine (25). However, in continuous hydrogenation of sunflower oil over palladium-on-alumina with metal concentrations of 0.1%, 0.2%, 0.5%, 2.0% and 5.0%, the maximum selectivity was obtained at 2.0% palladium (26).

Modified Catalysts

In an effort to improve selectivity or better control formation of *trans* isomers, noble metal catalysts have been modified by incorporation of various additives. Selectivity is generally somewhat improved, but any improvement in selectivity derived by changing an intrinsic property of the catalyst is off-set in part by the greater hydrogen availability at the catalyst surface resulting from the usually lower rates of hydrogenation. Palladium-lead catalysts (27) were used to improve selectivity in hydrogenation of linolenic acid, but the solvent had a greater effect on selectivity than did variations in the catalysts. Platinum, palladium and rhodium catalysts prepared

in molten lithium (27) showed no higher selectivity than conventional catalysts. Palladium catalysts modified by the addition of silver and bismuth have shown increased selectivity but at the expense of reduced rate (1). Addition of small amounts of platinum or rhodium to palladium-on-alumina increased the rate of hydrogenation of cottonseed oil, but minimum amounts of saturated material were formed over palladium alone (13).

An unusual type of selective catalyst that, judging by its behavior with small molecules, might prove quite useful in special hydrogenations of fats is sulfided platinum, palladium and rhodium catalysts (Engelhard Ind., Newark, N.J.). This type of catalyst shows very high selectivity in hydrogenation of dienes, like butadiene, admixed with other olefins and with nonconjugated dienes (29). Apparently no attempts have been made in the natural oils area to use these catalysts in selective hydrogenation of conjugated dienes in the presence of other types of unsaturation. Sulfided catalysts are inactive under mild conditions, and elevated temperatures and pressure have to be used for successful reductions.

Support

The properties of noble metal catalysts are modified to some extent by the support on which they are placed, but with some exceptions the variations in properties achieved on different supports are much less than the differences among the metals themselves. For instance, in selective hydrogenation of soybean oil over palladium and platinum on molecular sieves the catalysts were judged no more selective than conventional catalysts (3). Palladium and platinum supported on alumina did not differ appreciably from the metals supported on carbon (22). The effect of barium sulfate on suppressing *trans* isomer formation, noted earlier, had little effect on selectivity (11). One might anticipate that the effect of support on selectivity will be greatest when selectivity involves two different types of functional groups or when the functions differ in polarity from each other or from the molecule as a whole or when the reduction is sensitive to acids or bases. Some rather striking variations in selectivity due to the support have been recorded for molecules of this sort (31). In certain molecules the support may determine whether or not the reaction goes at all; catalytic hydrogenolysis of *cis*-6, 7-epoxyoctadecanoic acid over 10% palladium-on-carbon in ethanol gave nonselectively about equal amounts of the 6- and 7-hydroxyoctadecanoic acids, whereas over palladium-on-calcium carbonate the reaction failed (32).

Commercial Applications of Noble Metal Catalysts

Economic considerations dictate that commercial applications of noble metals catalysts be limited to palladium or to palladium admixed with small amounts of other noble metals as promoters. Palladium and ruthenium are roughly comparable in price whereas the other noble metal catalysts are more costly. But inasmuch as palladium is also the most active of the metals the economic choice happily coincides with the technical one. Palladium has been estimated to be from 30 (33) to 80-100 times (34) more active than nickel in hydrogenation of oils.

The two major technical problems connected with processing over palladium catalysts are the maintenance of a sufficiently clean system and the control of *trans* isomers in partially hydrogenated oils. Be-

cause palladium is so exceedingly active only very small amounts are needed, but the catalyst becomes sensitive to poisons. Modern processing methods usually provide feeds of sufficient purity to be used with palladium. Hydrogenations over palladium tend to produce relatively large amounts of *trans* isomers, but the amount can be controlled satisfactorily by suitable process conditions. Adequate selectivity is achieved without difficulty for palladium is a highly selective catalyst and selectivity occurs almost automatically.

Zajcew worked out satisfactory and economic processing conditions for the use of palladium in the productions of margarine stocks (25) including hydrogenated whale oil (35), shortening (1,36) and cocoa-butter substitutes (37) as well as the technical products castor wax (38) hydrogenated tall oil distillate (39) partially hydrogenated tall oil fatty acids, and fully hydrogenated fatty acids of various origins (10). Palladium is especially useful in the hydrogenation of fatty acids for, unlike nickel, it does not form soaps.

Some measure of the efficiency of palladium in hydrogenation of natural oils may be obtained from reports on pilot plant studies directed at the production of shortening stocks. Palladium was reused repeatedly reaching a total of 545,000 parts of oil hydrogenated per part of palladium (36). Hydrogenation of a single batch of 15,500 lb. of soybean oil to produce margarine was carried out with 775 g of 5% palladium-on-carbon corresponding to 0.00055% palladium based on oil (25).

At the end of the plant processing the catalyst had lost 15% of its initial activity. So far palladium has not been adapted for large scale partial hydrogenations of natural oils; the amount of palladium needed is very small and plant equipment must be altered or designed to handle filtration and recovery of small amount of catalysts.

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[Received April 28, 1970]