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(54) Title: CATALYST COMPOSITION AND METHOD FOR SELECTIVE DEHYDROGENATION			
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{R}^1 - \text{C} - \text{C} - \text{R}^4 \\ \quad \\ \text{R}^2 \quad \text{R}^3 \end{array} \quad (1)$			
(57) Abstract A method for selective dehydrogenation of a compound, comprising contacting a compound of formula (I), wherein each R¹, R², R³ and R⁴ is independently selected from the group consisting of H, (C₁-C₂₀) alkyl, (C₃-C₂₀) cycloalkyl, (C₆-C₂₀) aryl, (C₇-C₂₀) alkylaryl, (C₇-C₂₀) aralkyl groups, as well as substituted (C₁-C₂₀) alkyl, (C₃-C₂₀) cycloalkyl, (C₆-C₂₀) aryl, (C₇-C₂₀) aralkyl and (C₇-C₂₀) arylalkyl moieties, optionally further substituted with -OR, wherein R is R¹, R², R³ or R⁴; and wherein R¹ and R² or R³ and R⁴ may be joined as part of a ring structure, at a dehydrogenation temperature in the presence of a catalyst comprising about 0.01 wt % - 19.9 wt % Pd and about 0.01 wt % - 19.9 wt % Cu on a carbon support, wherein the total amount of (Pd + Cu) on the support is about 0.02 wt % to 20 wt %, the weight ratio of Pd:Cu is about 1:1 to 10:1, and the carbon support has a surface area of at least about 100 m²/g and is essentially free of reactive sulfur. A selective dehydrogenation catalyst having the composition described <i>supra</i> is disclosed as is a method of preparing the same. This catalyst is highly selective for dehydrogenating a variety of substrates while minimizing the formation of unwanted hydrogenolysis by-products.			

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Description
CATALYST COMPOSITION AND
METHOD FOR SELECTIVE DEHYDROGENATION

This invention relates to a catalyst composition
5 which has been shown to be useful for the selective
catalytic dehydrogenation of a variety of organic
substrates.

BACKGROUND OF THE INVENTION

Dehydrogenation reactions have been used to
10 effect aromatization as well as to place an olefinic
linkage in an open chain system (see, P. A. Plattner,
in "Newer Methods of Preparative Organic Chemistry",
Wiley Intersciences, New York, pp. 21-59 (1948);
Chem. Rev. 78: 317-361 (1978)). Two types of
15 reagents are most frequently used to effect
aromatization: (a) hydrogenation catalysts such as
platinum, palladium, nickel, etc., and (b) sulfur or
selenium which combine with the hydrogen evolved to
give H_2S or H_2Se .

20 Other reagents have also been used for
dehydrogenation, e.g., atmospheric oxygen, selenium
dioxide, quinones (see, Jackman, L.M., Org. Chem. 2:
329-366 (1960)) and activated charcoal (see, Shuikin
and Naryschkina, J. Prakt. Chem. [4] 13: 183 (1961)).

25 Dehydrogenation of open-chain systems to give a
double bond in a specific location is not usually a
feasible process, though industrially mixtures of
olefins are obtained in this way from alkanes.

There are few highly selective methods for
30 catalytic dehydrogenation. Competing secondary
reactions such as hydrogenolysis of carbon-oxygen

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bonds may occur detracting from the synthetic utility of this approach. For example, during the catalytic dehydrogenation of cyclohexylhydroquinone to phenylhydroquinone using a supported palladium catalyst,
5 large amounts of hydrogenolysis by-products such as 2- and 3-phenyl phenols are produced.

Thus, it is apparent there is still a need for a catalyst that will effect a selective dehydrogenation of substrates that are susceptible to hydrogenolysis.

10

SUMMARY OF THE INVENTION

A catalyst composition has now been discovered that can be used for the selective dehydrogenation of a variety of substrates. A unique feature of this catalyst is the high degree of selectivity obtained
15 thus avoiding the formation of unwanted reaction by-products.

The catalyst composition of the invention comprises

about 0.01 - 19.9 wt % Pd, and
20 about 0.01 - 19.9 wt % Cu,

on a carbon support, wherein the total amount of (Pd + Cu) on the support is about 0.02 wt % to 20 wt %, the weight ratio of Pd:Cu is about 1:1 to 10:1 and the carbon support has a surface area of at least
25 about 100 m²/g and is essentially free of reactive sulfur.

The catalyst of the invention is prepared by a method comprising

heat-treating a carbon support having a
30 surface area of at least about 100 m²/g at a

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temperature and for a time sufficient to remove essentially all volatile sulfur therefrom;

contacting the heat-treated carbon support with at least one Pd- source selected from the group consisting of palladium and anion-containing compounds of palladium and at least one Cu- source selected from the group consisting of copper and anion-containing compounds of copper in amounts effective to attain on the support a final amount of 0.01 - 19.9 wt % Pd and 0.01 - 19.9 wt % Cu, a total amount of (Pd + Cu) of about 0.02 wt % to 20 wt %, and a weight ratio of Pd:Cu of about 1:1 to 10:1. The catalyst is calcined prior to use under conditions effective to decompose the Pd- and Cu-containing compounds employed for catalyst preparation. Preferably, calcination will be carried out under conditions effective to remove substantially all the anions of the Pd- and Cu-containing compounds but not sufficient to cause excessive combustion of the carbon support.

This invention also relates to a method of dehydrogenating a compound, comprising contacting a compound of the formula



wherein each R^1 , R^2 , R^3 and R^4 is independently selected from the group consisting of

H, (C_1 - C_{20}) alkyl, (C_3 - C_{20}) cycloalkyl, (C_6 - C_{20}) aryl, (C_7 - C_{20}) alkylaryl, and

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(C₆-C₂₀) arylalkyl groups, as well as substituted (C₁-C₂₀) alkyl, (C₃-C₂₀) cycloalkyl, (C₆-C₂₀) aryl, (C₇-C₂₀) alkylaryl and (C₆-C₂₀) arylalkyl groups; each
5 such group optionally further substituted with -OR, wherein R is R¹, R², R³ or R⁴; and wherein R¹ and R² or R³ and R⁴ may be joined as part of a ring structure,

under dehydrogenation conditions in the presence of a
10 catalyst comprising about 0.01 wt % - 19.9 wt % Pd, and about 0.01 wt % - 19.9 wt % Cu on a carbon support, wherein the total amount of (Pd + Cu) on the support is about 0.02 wt % to 20 wt %, the weight ratio of Pd:Cu is about 1:1 to 10:1 and the carbon
15 support has a surface area of at least about 100 m²/g and is essentially free of reactive sulfur.

When palladium supported on an inert support in the absence of any amounts of copper is utilized as a dehydrogenation catalyst, large amounts of
20 hydrogenolysis by-products are obtained. One such example is the dehydrogenation of cyclohexylhydroquinone in which by-products such as 2- and 3-hydroxybiphenyls are evolved.

On the other hand, when the dehydrogenation
25 reaction is conducted utilizing the catalyst of this invention a selective dehydrogenation occurs and substantially no by-products are produced. Thus, when cyclohexylhydroquinone is dehydrogenated according to the inventive method it yields phenyl-
30 hydroquinone substantially in the absence of hydrogenolysis biphenyl by-products (see Example 1).

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Other objects, advantages and features of the present invention will become apparent to those skilled in the art from the following discussion and appended claims.

5 DETAILED DESCRIPTION OF THE INVENTION

The dehydrogenation method of the present invention is conducted with the aid of a mixed metal catalyst composition comprising palladium and copper supported on a carbon support.

10 The catalyst composition of the invention comprises

about 0.01 - 19.9 wt % Pd, and
about 0.01 - 19.9 wt % Cu,

on a carbon support, wherein the total amount of (Pd
15 + Cu) on the support is about 0.02 wt % to 20 wt %, the weight ratio of Pd:Cu is about 1:1 to 10:1 and the carbon support has a surface area of at least about 100 m²/g and is essentially free of reactive sulfur.

20 A preferred catalyst composition comprises about 5 wt % to 8 wt % of palladium and about 0.5 wt % to 2.5 wt % of copper on carbon. An extremely efficient, and thus a most preferred, catalyst is attained when a palladium:copper ratio is utilized
25 which is between about 3.0:1 and 4.0:1.

The catalyst composition of the invention is prepared by the method described supra. The contacting of the carbon support with the Pd- and Cu-containing compounds may be conducted by techniques
30 which are standard in the art, such as for example,

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aggregation, precipitation onto a support, evaporation of a metal-containing solution onto a support and the like. By means of example, the catalyst of the invention is prepared by dissolving appropriate

5 amounts of at least one palladium- and anion-containing compound and at least one Cu- and anion-containing compound in a solvent, the amounts being sufficient to attain a desired metal loading on a carbon support and the solution is added to the

10 carbon support material which has been heated to remove any volatile sulfur content at, e.g., about 700°C - 900°C. The solvent may be water, although the use of other solvents is also contemplated. Any excess solvent may be removed by methods known in the

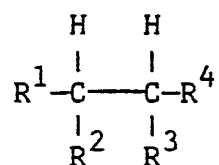
15 art, and the sample is then dried. The catalyst is then calcined prior to use to remove any anions present.

The Pd- and Cu-containing compounds employed for catalyst preparation are compounds where the metals

20 are associated with an anion. Any anion which may be removed by calcination or does not detract from the activity of the finished catalyst is suitable for the preparation of the present catalyst.

In accordance with another embodiment of the

25 present invention, a method is provided for dehydrogenation compounds of the formula

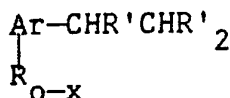


30 wherein each R^1 , R^2 , R^3 and R^4 is independently selected from the group consisting of

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H, (C₁-C₂₀) alkyl, (C₃-C₂₀) cycloalkyl,
 (C₆-C₂₀) aryl, (C₇-C₂₀) alkylaryl, and
 (C₇-C₂₀) arylalkyl groups, as well as
 substituted (C₁-C₂₀) alkyl, (C₃-C₂₀)
 5 cycloalkyl, (C₆-C₂₀) aryl, (C₇-C₂₀)
 alkylaryl and (C₆-C₂₀) arylalkyl groups; each
 such group optionally substituted with -OR,
 wherein R is R¹, R², R³ or R⁴; and
 wherein R¹ and R² or R³ and R⁴ may be
 10 joined as part of a ring structure.

A number of classes of compounds fall within this
 broad definition, e.g., straight chain alkanes having
 2 up to 20 carbon atoms, branched chain alkanes
 having 4 up to 20 carbon atoms, alkaryl compounds
 15 such as, for example, compounds of the formula:



wherein each R is independently selected from the
 group consisting of

20 -OZ, wherein Z=H,

C₁-C₂₀ alkyl,
 C₃-C₂₀ cycloalkyl,
 C₄-C₂₀ aromatic or hetero-
 aromatic moiety,

25 -OC(=O)-R', wherein R' = C₁-C₂₀ alkyl, or

C₃-C₂₀ cycloalkyl;

-COY, wherein Y=H

30

C₁-C₂₀ alkyl, or

C₃-C₂₀ cycloalkyl;

-C(=O)-Y, wherein Y is as defined above,

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$-\text{SO}_y\text{Z}'$, wherein Z' is C_1-C_{20} alkyl or
 C_2-C_{20} cycloalkyl;

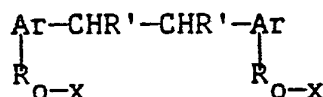
and $y=1$ or 2 ;

wherein each R' is independently H , C_1-C_{20} alkyl,
 5 C_3-C_{20} cycloalkyl, C_4-C_{20} aromatic or
 heteroaromatic moiety;

wherein Ar is an aromatic moiety having 6 up to 14
 carbon atoms;

wherein x is 4 when Ar has 6 carbons, x is 6 when Ar
 10 has 10 carbons and x is 8 when Ar is 14;

and diaryl ethanes of the formula:



wherein each R is independently selected from the
 15 group consisting of

$-\text{OZ}$, wherein $\text{Z}=\text{H}$,

C_1-C_{20} alkyl,

C_3-C_{20} cycloalkyl, or

20 C_4-C_{20} aromatic or hetero-
 aromatic moiety;

$-\text{OC}(=\text{O})-\text{R}'$, wherein $\text{R}' = \text{C}_1-\text{C}_{20}$ alkyl, or

C_3-C_{20} cycloalkyl;

25 $-\text{COY}$, wherein $\text{Y}=\text{H}$,

C_1-C_{20} alkyl, or

C_3-C_{20} cycloalkyl;

$-\text{C}(=\text{O})-\text{Y}$, wherein Y is as defined above,

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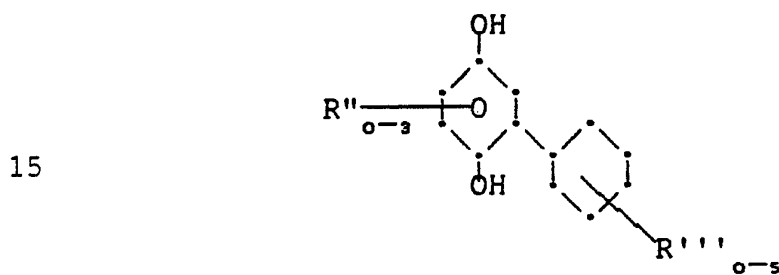
$-\text{SO}_y\text{Z}'$, wherein Z' is C_1-C_{20} alkyl or
 C_2-C_{20} cycloalkyl;

and $y=1$ or 2 ;

wherein each R' is independently H , C_1-C_{20} alkyl,
 5 C_3-C_{20} cycloalkyl, C_4-C_{20} aromatic or hetero-
 aromatic moiety;

wherein Ar is an aromatic moiety having 6 up to 14
 carbon atoms;

wherein x is 4 when Ar has 6 carbons, x is 6 when Ar
 10 has 10 carbons and x is 8 when Ar is 14; as well as
 phenols, hydroquinones of the structure:

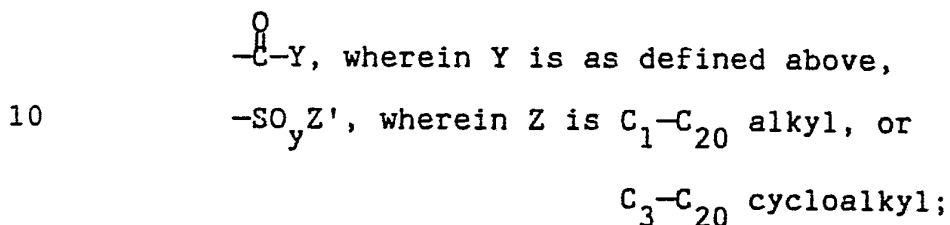
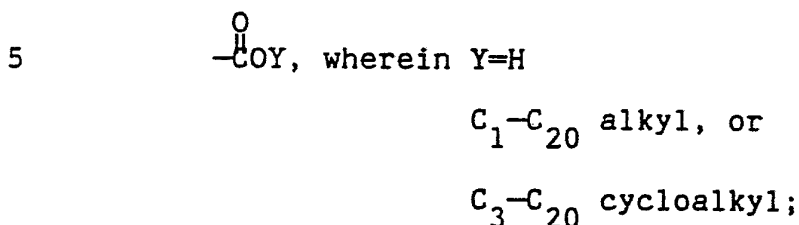
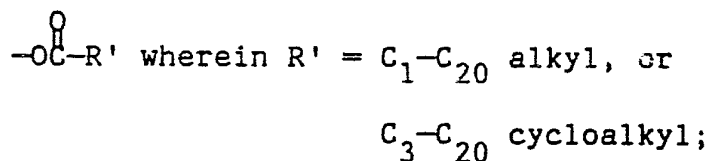


wherein each R'' is independently C_1-C_{20}
 alkyl, C_3-C_{20} cycloalkyl, C_4-C_{20} aromatic
 20 or heteroaromatic moiety; and wherein each R'''
 is independently

C_1-C_{20} alkyl,
 C_3-C_{20} cycloalkyl,
 C_6-C_{12} aryl,
 25 C_7-C_{20} aralkyl or alkaryl,
 $-\text{OZ}$, wherein $\text{Z}=\text{H}$,

C_1-C_{20} alkyl,
 C_3-C_{20} cycloalkyl,
 C_4-C_{20} aromatic or
 30 heteroaromatic moiety,

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and y=1 or 2.

and the like.

Exemplary compounds which are included in the

15 scope of dehydrogenatable compounds include cyclohexylhydroquinone and substituted derivatives thereof, 1,2-diphenylethane and substituted derivatives thereof, ethylbenzene and substituted derivatives thereof, alkanes such as propane, butane,

20 pentane, hexane, heptane, octane, nonane and decane.

The dehydrogenation reaction according to the present method is preferably conducted at a temperature ranging from between about 100°C to 400°C. A still more preferred range of temperatures

25 is between about 150°C and 300°C. The reaction is preferably conducted at atmospheric pressure, although other pressures are also contemplated herein.

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The dehydrogenation reaction of the present method may be conducted in either a fixed bed or a slurry reactor. When the reaction is conducted in a slurry reactor, the catalyst utilized in the present method may be recycled from the slurry by filtering the hot reaction mixture. The filtration may be conducted at the reaction temperature, above the melting point of the reaction mixture or at a temperature between 100°C and 200°C. A preferred range of temperatures for recovering the catalyst by filtration is between about 125°C and 150°C.

In a preferred embodiment of the invention, hydrogen gas produced as a result of the reaction is removed from the reaction atmosphere as the reaction proceeds. This can be accomplished by a variety of techniques as are well known by those of skill in the art. For example, the removal of hydrogen gas can be attained by circulating an inert gas through the atmosphere immediately above, or directly into, the reaction mixture. By means of example, the inert gas may be nitrogen. However, other unreactive gases may also be utilized for the removal of the hydrogen gas. As one alternative, hydrogen gas can be removed by careful addition of a purge gas containing small amounts of oxygen, which enables the removal of hydrogen as water.

The net result of hydrogen gas removal is to shift the equilibrium concentration from the starting material or substrate to the product of the reaction by removing from the system any amount of hydrogen produced.

The selective dehydrogenation reaction of this invention may be conducted for a period of time which varies with the substrate, desired percent conversion to product, mode of operation, etc. The time may

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vary in the range of about 1 minute up to 32 hours. In a fixed bed reactor, for example, reaction times of one minute or less may be suitable to achieve acceptable conversion levels, while in slurry or
5 stirred tank reactors, reaction times of several hours or more may be required to achieve acceptable conversion levels. It is recognized, of course, that an artisan may, without undue experimentation, adjust the period of time for the reaction to proceed by
10 following the progress of the reaction under specific conditions. The progress of the reaction may be monitored by appropriate known analytical techniques, e.g., by extracting aliquots from the reaction mixture at different times for analysis by gas chromatography.
15

The selective hydrogenation reaction of this invention may be optionally conducted in the presence of a solvent. Suitable solvents for use with the present method are solvents which are stable under
20 reaction conditions. Examples of suitable solvents are biphenyl, naphthalene, diphenylether, tetralin, durene, prehnitene or 1,2,3,4-tetramethylbenzene, and the like.

When the dehydrogenation reaction is completed,
25 the dehydrogenated product may be isolated from the reaction mixture (including the catalyst), and then further purified, by employing any of a variety of techniques readily available to those of skill in the art, e.g., by filtration, distillation, and the
30 like.

Having now generally described this invention, the same will be better understood by reference to the following examples, which are included herein for purposes of illustration only, and are not intended

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to be limiting of the invention or any embodiment thereof.

EXAMPLES

Catalyst employed in the examples which follow
5 was prepared according to the general procedure set forth below:

A carbon support material is heated to remove any residual volatile sulfur content. This is done at 700°-900°C (in a hydrogen flow) for eight hours prior
10 to metal addition. Appropriate amounts of palladium and copper nitrates necessary to achieve the desired metal loading are dissolved in water and the resulting solution added to the carbon support. Excess solvent is then removed by heating at 90°C in air for
15 several hours. Once the sample is dry, the materials are calcined in flowing air (i.e., a gas hourly space velocity (GHSV) in excess of about 1000/hr.) at 350°C for four hours prior to use.

20 Example 1 - Dehydrogenation of Cyclohexylhydroquinone
According to the Prior Art and the Invention Method

The following is a small scale reaction which is representative of the invention method, which can also be successfully conducted on a large scale.

25 A 250-ml 3-neck flask was fitted with a tube for the subsurface addition of gas, a mechanical stirrer, a thermometer and a condenser.

A sample for Test I was prepared by adding to the flask 100 g biphenyl, 20 g cyclohexylhydroquinone and
30 2.0 g of a catalyst containing 5 wt % Pd, 1.5 wt % Cu on carbon; then the flask was heated to 250°C. During the course of the reaction, nitrogen gas was

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incorporated into the reaction atmosphere by sub-surface addition thereof. After stirring the mixture for 24 hours at 250°C, an aliquot of the reaction mixture was analyzed by gas chromatography and found to contain 85% phenylhydroquinone and 10% cyclohexylhydroquinone as well as 3.2% hydrogenolysis by-products. This experiment is representative of the invention method.

The same procedure was conducted in the presence of 5% Pd on carbon but without copper (Test II). The reaction mixture was found to contain 90% hydrogenolysis by-products and only 10% phenylhydroquinone. This experiment is representative of the prior art.

The results of these tests are summarized in Table 1.

Table 1

Dehydrogenation Method Using Prior Art
and Invention Catalyst

Test	Dehydrogenation Catalyst			Products Obtained		
	Pd	Cu	Carbon	Cyclohexylhydroquinone	Phenylhydroquinone	Hydrogenolysis by-products
I	Yes	Yes	Yes	10%	85%	3.2%
II	Yes	No	Yes	—	10%	90%

The above results indicate the superiority (high selectivity for dehydrogenation) of the invention method conducted with a catalyst containing palladium and copper on a carbon support (Test I) when compared

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with the prior art method conducted with a catalyst containing only palladium on a carbon support (Test II).

5 Example 2 - Preparation of Phenylhydroquinone in a Slurry Reactor

The previous example was repeated with invention catalyst employing the following procedure:

10 To a four-neck round bottom flask fitted with a mechanical stirrer, condenser, thermometer and tube for subsurface nitrogen addition were added 100 g biphenyl, 20.0 g cyclohexylhydroquinone and 2.0 g of a catalyst containing 5 wt % palladium and 1.5 wt % copper on carbon. The reaction mixture was heated to 250°C with 0.5 SCFH subsurface addition of nitrogen
15 and was stirred at 250°C for 24 hours. The reaction mixture was then cooled to 150°C and the catalyst removed by filtration through a sintered glass funnel. The catalyst can be recycled back for another run without further purification or
20 treatment. The product filtrate analyzed by gas chromatography contained the following:

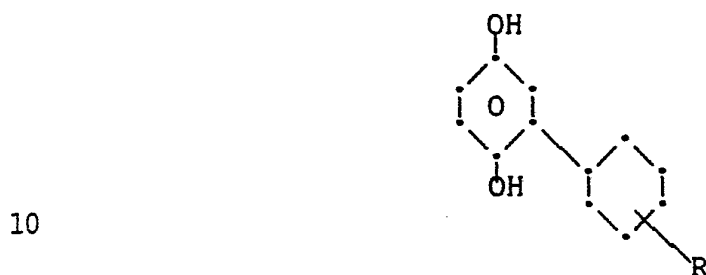
82.4 wt % phenyl hydroquinone,
8.3 wt % cyclohexyl hydroquinone,
0.7 wt % 2-phenylphenol,
25 2.0 wt % 3-phenylphenol, and
2.4 wt % hydroxydibenzofuran.

The phenylhydroquinone can be isolated in high yield and in pure form by vacuum distillation (the boiling point of phenylhydroquinone at 2.0 mm is
30 187°C).

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Example 3 - Dehydrogenation of Substituted Cyclohexylhydroquinones With the Catalyst of the Invention

A variety of substituted cyclohexylhydroquinones
5 of the formula



wherein R is -H, -CH₃, -C₆H₅, -OCH₃ and
-OCO-CH₃ (-OAc) were dehydrogenated to the
corresponding substituted phenylhydroquinones
15 employing the procedure set forth in Example I. The
catalyst employed was 5 wt % Pd and 1.5 wt % Cu on
carbon. The reaction was conducted at 250°C with
biphenyl as a solvent. The results of the
experiments are set forth in Table 2.

20

Table 2

Dehydrogenation of Substituted
Cyclohexylhydroquinones With Invention Catalyst

	R	Conversion	Selectivity
		(%)	(%)
25	-H	88	90
	p-CH ₃	90	92
	p-C ₆ H ₅	95	92
	p-OCH ₃	90	90
	p-OAc	75	90

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The results of these experiments demonstrate that the invention method employing Pd-Cu on carbon support is effective for the conversion of a variety of substituted cyclohexylhydroquinones to produce a high yield of the corresponding substituted phenylhydroquinones. Selectivities to the desired phenylhydroquinone in all cases were 90% or greater, with conversions of at least 75%. It is especially noteworthy that essentially no hydrogenolysis occurred in any of these dehydrogenation reactions.

Example 4 - Comparison of Invention Catalyst with Other Catalysts

A series of experiments were carried out to compare the conversion of cyclohexylhydroquinone to phenylhydroquinone employing the palladium-copper on carbon catalyst of this invention, and employing prior art dehydrogenation catalysts. The experiments were all run at 250°C in biphenyl as a solvent employing the procedure set forth in Example I.

The results of the experiments are set forth in Table 3.

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Table 3

Comparison of Invention Catalyst with Prior Art Catalysts for the Dehydrogenation of Cyclohexylhydroquinone

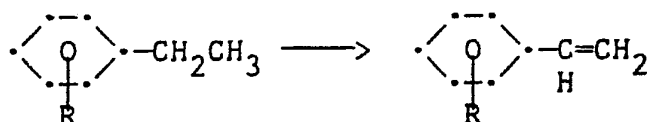
5	Catalyst	Conversion (%)	Selectivity (%)
	5% Pd/carbon	100	4
	5% Pt/carbon	99	20
	8% Pd, 2% Pt/carbon	95	42
10	5% Rh/carbon	37	69
	5% Pd, 1.5% Cu/carbon	88	90
	5% Pd, 0.8% Ag/carbon	72	57
	5% Pd, 2.5% Cu/Al ₂ O ₃	20	65
	5% Pd, 2.5% Cu/SiO ₂	12	82
15	5% Pd, 2.5% Cu/carbon	43	99

Several prior art catalysts (e.g., Pd/C, Pt/C and Pd-Pt/C) give high levels of cyclohexylhydroquinone conversion, but selectivities to the desired product, phenylhydroquinone, are quite poor. Similarly, other prior art catalyst systems suffer from either low conversion levels, or poor selectivity, or both. Only invention catalyst containing Pd and Cu on carbon support are capable of giving yields of desired product.

25 Example 5 - Selective Dehydrogenation of Substituted Ethyl Benzenes to the Corresponding Styrenes with the Catalyst of the Invention

30 A series of substituted ethyl benzenes was dehydrogenated to the corresponding styrenes according to the following chemical reaction:

- 19 -



wherein R is -H, p-OH, p-OCH₃ and m-OCH₃.

5 These reactions were all carried out at 200°C in
100 g biphenyl solvent in the apparatus described in
Example I with 2 g of 5 wt % Pd and 2.5 wt % Cu on
carbon as the catalyst and 20 g of ethyl benzene
substrate. The results of these experiments are set
10 forth in Table 4.

Table 4

Selective Dehydrogenation of Substituted
Ethyl Benzenes

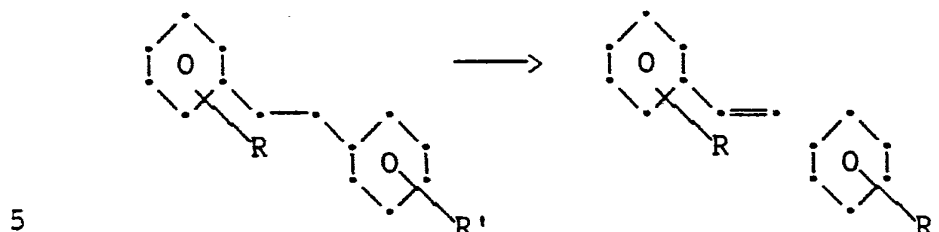
15	R	Conversion	Selectivity
		(%)	(%)
	-H	95	92
	p-OH	97	90
	p-OCH ₃	92	91
	m-OCH ₃	90	92

20 In all cases, good yields (greater than 90%
conversion and 90% selectivity) were obtained with a
variety of substituted ethyl benzenes, thereby
selectively producing a variety of substituted
styrenes in high yield.

25 Example 6 - Selective Dehydrogenation of Substituted
1,2-diphenylethanes to the Corresponding
Stilbenes

A series of substituted 1,2-diphenylethanes were
dehydrogenated to the corresponding stilbenes accord-
30 ing to the following reaction.

- 20 -



wherein each of R or R' is independently -H, p-OH, p-OCH₃ and p-COOCH₃.

These reactions were all conducted at 250°C in the presence of 2 g of a 5 wt % Pd, 2.5 wt % Cu on carbon catalyst and 100 g biphenyl as a solvent, with 20 g of 1,2-diphenyl ethane substrate. The results of the experiments are set forth in Table 5.

Table 5

15

Selective Dehydrogenation of Substituted 1,2-Diphenylethanes			
R	R'	Conversion (%)	Selectivity (%)
-H	-H	92	96
p-OH	-H	90	92
20 p-OCH ₃	p-OH	95	90
p-OH	p-OH	88	86
p-COOCH ₃	p-COOCH ₃	82	90

The results demonstrate that the invention Pd-Cu on carbon catalyst is effective for the selective dehydrogenation of diphenylethanes to produce stilbenes.

25

- 21 -

Example 7 - Dehydrogenation of n-Butane

The dehydrogenation of n-butane was conducted in the gas phase at 180°C and 280°C using a 8 wt % Pd, 2.5 wt % Cu on carbon catalyst. 3.8 g of the catalyst in powder form were placed in a plug flow microreactor and heated to reaction temperature in a flow of nitrogen gas. Once the reaction temperature was achieved, n-butane was fed to the catalyst bed at 170 SCCM and the amount of the products obtained at the two temperatures were monitored by gas chromatography. The results of these experiments are set forth in Table 6.

Table 6

Dehydrogenation of n-butane at
Different Temperatures

Temp. (°C)	Products (mole%)					
	CH ₄	i-butane	1-butene	c-butene	t-butene	1,3-butadiene
180	0.21	0.22	0.00	0.20	0.36	0.00
280	0.01	0.14	0.14	0.39	0.24	0.08

These results demonstrate that the invention Pd-Cu on carbon catalyst is effective for the dehydrogenation of saturated hydrocarbons such as butane, to produce unsaturated compounds. Note that at low reaction temperatures, high selectivity to the internal alkene, 2-butene, is obtained.

The invention now being fully described, it will be apparent to one of ordinary skill in the art that

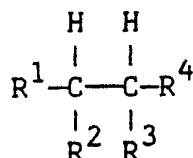
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many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

- 23 -

ClaimsWe Claim

1. A method for the selective dehydrogenation of a compound, comprising dehydrogenating a compound of the formula



- wherein each of R^1 , R^2 , R^3 and R^4 is independently selected from the group consisting of H, $(\text{C}_1 - \text{C}_{20})$ alkyl, $(\text{C}_3 - \text{C}_{20})$ cycloalkyl, $(\text{C}_6 - \text{C}_{20})$ aryl, $(\text{C}_7 - \text{C}_{20})$ alkylaryl, and $(\text{C}_7 - \text{C}_{20})$ aralkyl groups, and substituted $(\text{C}_1 - \text{C}_{20})$ alkyl, $(\text{C}_3 - \text{C}_{20})$ cycloalkyl and $(\text{C}_6 - \text{C}_{20})$ aryl, $(\text{C}_7 - \text{C}_{20})$ alkylaryl and $(\text{C}_7 - \text{C}_{20})$ aralkyl; each such group optionally substituted with $-\text{OR}$, wherein R is R^1 , R^2 , R^3 or R^4 ; and wherein R^1 and R^2 or R^3 and R^4 may be joined as part of a ring structure, at a dehydrogenation temperature in the presence of a catalyst comprising about 0.01 wt % - 19.9 wt % Pd, and about 0.01 wt % - 19.9 wt % Cu on a carbon support, wherein the total amount of (Pd + Cu) on the support is about 0.02 wt % to 20 wt %, the weight ratio of Pd:Cu is about 1:1 to 10:1, and the carbon support has a surface area of at least about $100 \text{ m}^2/\text{g}$ and is essentially free of reactive sulfur.
2. The method of Claim 1, wherein the dehydrogenating step is conducted in the presence of a

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- 5 catalyst consisting essentially of about 0.01 wt % - 19.9 wt % Pd and about 0.01 wt % - 19.9 wt % Cu on a carbon support, wherein the total amount of (Pd + Cu) on the support is about 0.02 wt % to 20 wt %, the weight ratio of Pd:Cu is about 1:1 to 10:1 and the carbon support has a surface area of at least about 100 m²/g and is essentially free of reactive sulfur.
- 10 3. The method according to Claim 1, wherein the palladium:copper ratio is about 3.0:1 to 4.0:1.
4. The method according to Claim 1, wherein the dehydrogenating temperature is about 100°C to 400°C.
- 15 5. The method according to Claim 1, wherein the dehydrogenation is conducted in the presence of a reaction solvent.
- 20 6. The method according to Claim 5, wherein the reaction solvent is selected from the group consisting of biphenyl, naphthalene, diphenyl ether, tetralin, durene and prehnitene.
7. The method according to Claim 6, wherein the solvent is biphenyl.
- 25 8. The method according to Claim 1, further comprising constantly removing hydrogen gas produced in the dehydrogenation step.
9. The method according to Claim 8, wherein the hydrogen gas is removed by circulating an inert gas.

- 25 -

10. The method according to Claim 8 wherein the hydrogen is removed by reaction with controlled levels of oxygen added to the dehydrogenation reaction zone.
- 5 11. The method according to Claim 1 wherein the compound to be dehydrogenated is a straight chain alkane having 2 up to 20 carbon atoms.
12. The method according to Claim 11 wherein the compound to be dehydrogenated is selected from
10 the group consisting of:
- propane,
butane,
pentane,
hexane,
15 heptane,
octane,
nonane, and
decane.
13. The method according to Claim 11 wherein the
20 compound to be dehydrogenated is selected from the group consisting of propane and butane.
14. The method according to Claim 1 wherein the compound to be dehydrogenated is a branched chain alkane having 4 up to 20 carbon atoms.
- 25 15. The method according to Claim 14 wherein the compound to be dehydrogenated is selected from the group consisting of branched chain alkanes having 4 up to 12 carbon atoms.

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16. The method according to Claim 1 wherein the compound to be dehydrogenated is an alkyl aromatic compound of the formula



wherein each R is independently selected from the group consisting of

-OZ, wherein Z=H,

- $\text{C}_1\text{-C}_{20}$ alkyl,
 $\text{C}_3\text{-C}_{20}$ cycloalkyl,
 $\text{C}_4\text{-C}_{20}$ aromatic or hetero-
 aromatic moiety,

$-\text{OC}(=\text{O})\text{-R}'$, wherein $\text{R}' = \text{C}_1\text{-C}_{20}$ alkyl, or
 $\text{C}_3\text{-C}_{20}$ cycloalkyl;

$-\text{COY}$, wherein Y=H

$\text{C}_1\text{-C}_{20}$ alkyl, or

$\text{C}_3\text{-C}_{20}$ cycloalkyl;

$-\text{C}(=\text{O})\text{-Y}$, wherein Y is as defined above,

$-\text{SO}_y\text{Z}'$, wherein Z' is $\text{C}_1\text{-C}_{20}$ alkyl or
 $\text{C}_2\text{-C}_{20}$ cycloalkyl;

and y=1 or 2;

wherein each R' is independently H, $\text{C}_1\text{-C}_{20}$
 alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_4\text{-C}_{20}$ aromatic
 or heteroaromatic moiety;

wherein Ar is an aromatic moiety having 6 up to 14 carbon atoms;

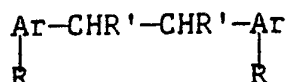
wherein x is 4 when Ar has 6 carbons, x is 6 when
 Ar has 10 carbons and x is 8 when Ar is 14.

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17. The method according to Claim 16 wherein the compound to be dehydrogenated is selected from the group consisting of:

ethylbenzene,
 5 p-hydroxy ethylbenzene,
 p-methoxy ethylbenzene, and
 m-methoxy ethylbenzene.

18. The method according to Claim 1 wherein the compound to be dehydrogenated is a 1,2-diaryl ethane of the formula:



wherein each R is independently selected from the group consisting of

15 -OZ, wherein Z=H,

C_1-C_{20} alkyl,

C_3-C_{20} cycloalkyl,

C_4-C_{20} aromatic or hetero-
aromatic moiety,

20 $-\text{OC}(=\text{O})-\text{R}'$, wherein $\text{R}' = \text{C}_1-\text{C}_{20}$ alkyl, or

C_3-C_{20} cycloalkyl;

$-\text{C}(=\text{O})\text{OY}$, wherein Y=H

25 C_1-C_{20} alkyl, or

C_3-C_{20} cycloalkyl;

$-\text{C}(=\text{O})-\text{Y}$, wherein Y is as defined above,

$-\text{SO}_y\text{Z}'$, wherein Z' is C_1-C_{20} alkyl or
 C_2-C_{20} cycloalkyl;

30

and $y=1$ or 2 ;

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wherein each R' is independently H, C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₄-C₂₀ aromatic or heteroaromatic moiety;

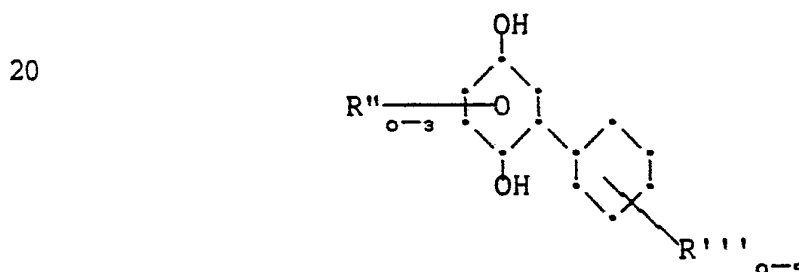
5 wherein Ar is an aromatic moiety having 6 up to 14 carbon atoms;

wherein x is 4 when Ar has 6 carbons, x is 6 when Ar has 10 carbons and x is 8 when Ar is 14.

19. The method according to Claim 18 wherein the compound to be dehydrogenated is selected from the group consisting of:

1,2-diphenylethane,
1-phenyl-2-p-hydroxyphenylethane,
1,2-bis(p-hydroxyphenyl)ethane,
1,2-bis(methyl-p-benzoate)ethane, and
15 1-p-hydroxyphenyl-2-p-methoxyphenyl ethane.

20. The method according to Claim 1 wherein the compound to be dehydrogenated is a cyclohexyl hydroquinone compound of the formula:



25 wherein each R'' is independently C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₄-C₂₀ aromatic or heteroaromatic moiety; and wherein each R''' is independently

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- C_1-C_{20} alkyl,
 C_3-C_{20} cycloalkyl,
 C_6-C_{12} aryl,
 C_7-C_{20} aralkyl or alkaryl,
 5 -OZ, wherein Z=H,
 C_1-C_{20} alkyl,
 C_3-C_{20} cycloalkyl,
 C_4-C_{20} aromatic or
 heteroaromatic moiety,
- 10 $-OC(=O)R'$, wherein $R' = C_1-C_{20}$ alkyl, or
 C_3-C_{20} cycloalkyl;
- $-C(=O)Y$, wherein Y=H,
 C_1-C_{20} alkyl, or
 15 C_3-C_{20} cycloalkyl;
- $-C(=O)Y$, wherein Y is as defined above,
 $-SO_yZ'$, wherein $Z' = C_1-C_{20}$ alkyl, or
 C_3-C_{20} cycloalkyl;
- and y=1 or 2.

- 20 21. The method according to Claim 1 wherein the compound to be dehydrogenated is selected from the group consisting of:

- cyclohexylhydroquinone,
 4-methylcyclohexyl hydroquinone,
 25 4-phenylcyclohexyl hydroquinone,
 4-methoxycyclohexyl hydroquinone, and
 4-acetoxycyclohexyl hydroquinone,

- 30 -

22. The method according to Claim 20, wherein the compound to be dehydrogenated is cyclohexylhydroquinone.
23. The method according to Claim 22 wherein the
5 phenylhydroquinone obtained in the dehydrogenation step is substantially free of hydrogenolysis by-products.
24. A dehydrogenation catalyst composition consisting essentially of
- 10 about 0.01 wt % to 19.9 wt % Pd, and
about 0.01 wt % to 19.9 wt % Cu
- on carbon support, wherein the total amount of (Pd + Cu) on the support is about 0.02 wt % to 20 wt %, the weight ratio of Pd:Cu is about 1:1 to
15 10:1, and the carbon support has a surface area of at least about 100 m²/g and is essentially free of reactive sulfur.
25. A selective dehydrogenation catalyst comprising the composition of Claim 24.
- 20 26. A catalyst according to Claim 24 wherein the quantity of Pd varies in the range of about 5 up to 8 wt % and the quantity of Cu varies in the range of about 0.5 up to 2.5 wt %, and the weight ratio of Pd:Cu varies in the range of about 3.0:1
25 up to 4.0:1.
27. A method of preparing a selective dehydrogenation catalyst, said method comprising heat-treating a carbon support having a surface area of at least

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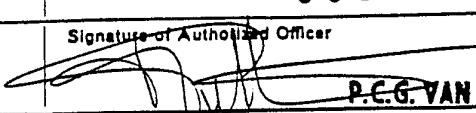
about 100 m²/g at a temperature and for a time sufficient to remove substantially all volatile sulfur therefrom; .

5 contacting the heat-treated carbon support with
at least one Pd- source selected from the group
consisting of palladium and anion-containing
compounds of palladium and at least one Cu-
source selected from the group consistng of
copper and anion-containing compounds of copper
10 in amounts effective to attain a final amount on
the support of 0.01 wt % to 19.9 wt % Pd and 0.01
wt % to 19.9 wt % Cu, a total amount of (Pd+Cu)
of about 0.02 wt % to 20 wt % and a weight ratio
of Pd:Cu of about 1.1 to 10.1.

15 28. The method of Claim 27, further comprising
calcining the Pd-Cu-contacted support under
conditions effective to decompose the Pd- and
Cu-containing compounds employed for catalyst
preparation, but not sufficient to cause
20 excessive combustion of the support.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 88/02426

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ B 01 J 23/89; C 07 B 35/04; C 07 C 5/00; C 07 C		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC ⁴	B 01 J; C 07 B; C 07 C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	Chemical Reviews, Volume 78, Number 4, August 1978 p 318-333 "Dehydrogenation of Polycyclic Hydroaromatic Compounds" (Peter P Fu et al) ---	1-28
A	DE, C2, 2602894 (DeThomas W R) 10 April 1986 ---	24-28
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
3rd November 1988	05 DEC 1988	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 P.C.G. VAN DER PUTTEN	

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EPO file on 17/10/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE- C2- 2602894	28-10-76	FR 2307578 GB 1534136 JP 51124689	12-11-76 29-11-78 30-10-76