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(72) de Agudelo, Magdalena Ramirez, VE

(72) Guerra, Julia, VE

(72) Romero, Trino, VE

(72) Medina, Mariela, VE

(73) INTEVEP, S.A., VE

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(54) **CATALYSEURS POUR L'HYDROGENATION SELECTIVE
SIMULTANEE DE DIOLEFINES ET DE NITRILES;
METHODE DE PREPARATION**

(54) **CATALYST FOR THE SIMULTANEOUS SELECTIVE
HYDROGENATION OF DIOLEFINS AND NITRILES AND
METHOD OF MAKING SAME**

(57) Catalyseur utile pour l'hydrogénation simultanée et sélective de dioléfines et de nitriles présents dans une charge d'alimentation d'hydrocarbures. Le matériau du support est choisi de préférence dans le groupe suivant : composite oxyde inorganique-zéolite, carbone et zéolite. Une phase à activité catalytique est déposée sur le matériau du support. La phase métallique à action catalytique est sélectionnée dans le groupe suivant : métaux du groupe IB partiellement réduits et métaux du groupe VIII entièrement réduits. La teneur en cette phase métallique à activité catalytique est d'environ $\geq 0,03$ % en poids.

(57) A catalyst useful for the simultaneous and selective hydrogenation of diolefins and nitriles present in a hydrocarbon feedstock. The support material is preferably selected from the group consisting of an inorganic oxide-zeolite composite, carbon and zeolite. A catalytically active phase is deposited on the support material. The catalytically active metal phase is selected from the group consisting of partially reduced Group IB metals and completely reduced Group VIII metals. The catalytically active metal phase is present in an amount of ≥ 0.03 wt%.

ABSTRACT

A catalyst useful for the simultaneous and selective hydrogenation of diolefins and nitriles present in a hydrocarbon feedstock. The support material is preferably selected from the group consisting of an inorganic oxide-zeolite composite, carbon and zeolite. A catalytically active phase is deposited on the support material. The catalytically active metal phase is selected from the group consisting of partially reduced Group IB metals and completely reduced Group VIII metals. The catalytically active metal phase is present in an amount of ≥ 0.03 wt%.

BACKGROUND OF THE INVENTION

The present invention relates to a catalyst material for use in the hydrogenation of hydrocarbon feedstocks and, more particularly, a catalyst which is useful for the simultaneous and selective hydrogenation of diolefins and nitriles present in a hydrocarbon feedstock.

There are known in the prior art processes in catalysts for hydrogenating unsaturated compounds in liquid hydrocarbon feedstocks. For example, U.S. Patent 4,152,351 discloses a process for the hydrogenation an olefinic unsaturation. More specifically, it relates to the catalytic hydrogenation of aliphatic, unsaturated compound in the presence of a palladium hydrogenation catalyst on a suitable support. Still more specifically, the invention relates to the use of applicable adjuvants for a palladium hydrogenation catalyst used to hydrogenate the olefinic unsaturation. Further, the invention relates to the hydrogenation of aliphatic, unsaturated compounds containing nitrile groups. U.S. Patent 4,271,323 discloses a process for hydrogenating unsaturated compounds in the liquid phase in the presence of a soluble catalyst obtained by reacting an organometal derivative or a metal hydride with a synergistic mixture of (a) a compound of zinc, zirconium, manganese, molybdenum, or iron and (b) a nickel or cobalt compound. U.S. Patent 4,734,540 discloses a process which

is useful for the selective hydrogenation of polyunsaturated organic compounds. The resultant product of such a reaction produces the monoolefinic equivalents of the hydrogenated polyunsaturated organic compounds. The catalyst used in this selective hydrogenation process comprises nickel and sulfur deposited on the surface of an alumina support. The preferred catalyst does not contain halogens, noble metals, alkaline earth metals, or alkali metals and is characterized by having only a very low percentage of the total pore volume being provided by pores having an average pore diameter less than 150 angstroms. The great majority of the pore volume is present in the form of macropores having diameters of 500 to 1500 angstroms.

While the foregoing processes employ catalysts which are useful in the hydrogenation process, the processes and catalysts are not as selective nor do they simultaneously hydrogenate diolefins and nitriles. Naturally, it would be highly desirable to provide a catalyst which is useful for the simultaneous selective hydrogenation of diolefins and nitriles in a hydrocarbon feedstock.

Accordingly, it is the principle object of the present invention to provide a catalyst useful for the simultaneous and selective hydrogenation of diolefins and nitriles present in a hydrocarbon feedstock.

It is a further object of the present invention to

provide a method for preparing a catalyst a aforesaid.

It is a still further object of the present invention to provide a process for the simultaneous and selective hydrogenation of diolefins and nitriles from a hydrocarbon feedstock employing such a catalyst.

Further objects and advantages of the present invention will appear hereinbelow.

SUMMARY OF THE INVENTION

The present invention relates to a catalyst useful for the simultaneous and selective hydrogenation of diolefins and nitriles present in a hydrocarbon feedstock. The support material is preferably selected from the group consisting of an inorganic oxide-zeolite composite, carbon and zeolite. A catalytically active phase is deposited on the support material. The catalytically active metal phase is selected from the group consisting of partially reduced Group IB metals and completely reduced Group VIII metals. The catalytically active metal phase is present in an amount of ≥ 0.03 wt%.

The catalyst of the present invention is particularly useful in a process for the simultaneous and selective hydrogenation of diolefins and nitriles present in a hydrocarbon feedstock. The catalyst of the present invention is prepared by impregnating the support material

with a solution of the active metal phase, drying the impregnated support and calcining. The dried and calcined support is thereafter activated to the proper reduction state. The catalyst is used in a hydrogenation process wherein the hydrocarbon feedstock in the presence of the catalyst and hydrogen is treated at a temperature of between about 50 to 250°C and a pressure of 150 to 650 psi so as to selectively hydrogenate diolefins and nitriles from the hydrocarbon feedstock.

DETAILED DESCRIPTION

The catalyst of the present invention is particularly useful in a process for the simultaneous selective hydrogenation of diolefins and nitriles.

The catalyst of the present invention comprises a support material having a catalytically active metal phase deposited thereon. Suitable support materials include inorganic oxide-zeolite composites, carbon and zeolite. A particular useful support material for use in the catalyst of the present invention is a composite alumina-zeolite material disclosed in U.S. Patent 4,762,537 and sold under the trademark Selexsorb by the Aluminum Company of America.

The support material has deposited thereon a catalytically active metal phase selected from the group consisting of Group IB metals and Group VIII metals of the

Periodic Table. Depending on the active metal employed, the amount of the metal active phase present on the catalyst may vary. The active metal should be present in a minimum amount of about ≥ 0.03 wt% up to 20 wt%. Particularly
5 suitable active metal materials include copper, nickel and palladium.

As noted above, particularly suitable support material for use in the catalyst of the present invention is an alumina-zeolite composite sold by the Aluminum Company of
10 America under the trademark Selexsorb. It has been found that the surface area of the resulting catalyst should be between about 100 to 1500 m²/g, preferably between 100 to 1000 m²/g and ideally between about 250 to 350 m²/g. The pore volume of the catalyst is preferably between 0.20 cc/g
15 to 1.50 cc/g, preferably 0.30 cc/g to 0.70 cc/g.

In order for the catalyst of the present invention to be effective in the simultaneous selective hydrogenation of diolefins and nitriles, it has been found that the metal active phase must be reduced to the right state in order to
20 be effective. In accordance with the present invention the Group IB metals must be partially reduced while the Group VIII metals must be completed reduced. By partial reduction it is meant that metal sites consist of one or more than one oxidation state different than zero, more particularly

catalyst exhibit metal sites with a net charge on them. By complete reduction it is meant the metal sites largely consist on a single species, more particularly the highest number of species exhibit the elemental state of charge, i.e., zero.

The catalyst of the present invention is prepared by impregnating the support material with a solution containing the catalytically active metal phase. As noted above the metal active phase should be present in an amount on the final catalyst of about ≥ 0.03 wt%. The impregnated support material is thereafter dried and calcined at a temperature of between 150 and 600°C for a time sufficient to decompose the metal salt impregnated on the catalyst support. Particularly suitable metal salts used in the aqueous solution for impregnating the catalyst material include $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$; $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $(\text{CH}_3\text{COO})_2\text{Pd}$. The dried and calcined catalyst is thereafter activated to the proper reduction state depending on the type of active metal phase employed. Partial reduction of the Group IB metals are accomplished under the following conditions: Temperature (°C) 150-300, Pressure (psi) 15-350, H_2 flow rate (lt/h) 0.1-8.0. Complete reduction of the Group VIII is achieved under the following conditions: Temperature (°C) 200-600, Pressure (psi) 15-350, H_2 flow rate (lt/h) 0.1-8.0.

The catalyst of the present invention prepared in accordance with the method described above is particularly useful in processes for the simultaneous and selective hydrogenation of diolefins and nitriles from a hydrocarbon feedstock. The hydrocarbon feedstock in the presence of the catalyst is mixed with hydrogen wherein the ratio of the hydrogen to the diolefins and nitriles in the feedstock is less than three times stoichiometric amount required to selectively hydrogenate diolefins and nitriles. The hydrogen, hydrocarbon feedstock and catalyst are treated in a reactor at a temperature of between 50 to 250°C at a pressure of between 150 to 650 psi. The preferred conditions for the hydrogenation process are a temperature of between 70 to 160°C at a pressure of between 200 to 400 psi at a liquid hourly space velocity of between 0.1 to 5 h⁻¹, preferably 0.5 to 5 h⁻¹, ideally 1 to 4.5 h⁻¹.

The advantageous features of the catalyst of the present invention and method for preparing same will become clear from the following examples.

EXAMPLE 1

This example demonstrates the process for making the catalyst of the present invention employing an inorganic oxide-zeolite composite support having a Group VIII

activated metal phase deposited thereon.

5 An alumina-zeolite composite support of the type
disclosed in U.S. Patent 4,762,537 and sold by Alcoa
Aluminum Corporation under the trademark Selexsorb was
selected as the catalyst support material. Four of the
catalysts supports were impregnated with solutions of nickel
nitrate of different concentrations. A fifth catalyst was
prepared by impregnating the catalyst support with
palladium. The five impregnated catalysts were dried and
10 calcined so as to decompose the salts of the incorporated
active metal. The calcined impregnated catalysts supports
were then activated under controlled temperature and time
conditions so as to completely reduce or partially reduce
the active metal phase. For complete reduction, the
15 catalysts were treated at a temperature of 450°C at 250 psi
for 8 hours. Partial reduction was carried out at 250°C for
8 hours at 200 psi. Table 1 below sets forth the catalyst
composition and activation treatment for each of the five
catalysts.

Table 1

Catalyst	Support	Active Metal	Phase	Activation

5	1	alumina-zeolite	0.93 wt% Ni	completely reduced
	2	alumina-zeolite	5.7 wt% Ni	completely reduced
	3	alumina-zeolite	5.7 wt% Ni	partially reduced
10	4	alumina-zeolite	12.90 wt% Ni	completely reduced
	5	alumina-zeolite	0.30 wt% Pd	completely reduced

EXAMPLE 2

15 This example demonstrates the catalyst activity for the catalysts of Example 1 for the simultaneous and selective hydrogenation of diolefins and nitriles present in hydrocarbon feedstocks.

20 The activity for the simultaneous selective hydrogenation was determined during a 4 hour run using a synthetic C5 hydrocarbon feedstock having the composition set forth below in Table 2.

Table 2Synthetic Feedstock Composition

C5	97.5%
Propilonitrile	0.5%
Diolefins	0.5%
Monoolefins	1.0%

Eight cc's of each of the activated catalysts set forth in Example 1 were employed in a reactor for treating the hydrocarbon feedstock of Table 2. The reaction took place for 3 hours at a temperature of 120°C and a pressure of 250 psi. The ratio by volume of hydrogen fed to the reactor with respect to the diolefins and nitriles was maintained at 3. The liquid space velocity (LHSV) of hydrogen feed was set at 3h⁻¹. The results for each run employing the catalysts of Example 1 are set forth herein below in Table 3.

Table 3

Catalyst	% Conversion Diolefins	%Conversion Monoolefins	%Conversion Nitriles
1	100	59	86
2	100	78	100
3	0	0	0
4	100	0	100
5	100	0	88

As can be seen from Table 3 the concentration of the active metal phase of the Group VIII metal employed have an affect on the selective hydrogenation of the diolefins and nitriles in the hydrocarbon. Nickel concentrations of below 6 wt% were insufficient to insure selective hydrogenation. Catalyst 1 having a nickel concentration of 0.93 wt% was in fact not selective. At the same time, as can be seen from the results employing catalyst 5, 0.3 wt% palladium is sufficient for insuring selective hydrogenation of diolefins and nitriles. In addition, when comparing the results obtained from hydrogenation of feedstocks with catalysts 4 and 3, it can be seen that the Group VIII metals must be completely reduced in order for the catalyst to be active for the hydrogenation of diolefins and nitriles. Specifically, catalyst 3 which contained 5.7 wt% nickel partially reduced did not achieve any conversion of either olefins, monoolefins or nitriles.

EXAMPLE 3

This example demonstrates the process for making the catalyst of the present invention employing an inorganic oxide-zeolite composite support having a Group IB active metal phase deposited thereon.

Three alumina-zeolite composite supports were impregnated with solutions of copper nitrate of different

concentrations. The three impregnated catalysts were dried and calcined so as to decompose the salts of the incorporated active metal. Two of calcined impregnated catalyst supports were activated by carrying out partial reduction of the active metal phase at 250°C for three hours. The third impregnated catalyst support was completely reduced under the same conditions set forth in Example 1. Table 4 below sets forth the catalyst composition and activation treatment for each of the four catalysts.

Table 4

Catalyst	Support	Active Metal Phase	Activation
6	alumina-zeolite	0.79 wt% Cu	partially reduced
7	alumina-zeolite	5.9 wt% Cu	partially reduced
8	alumina-zeolite	5.8 wt% Cu	completely reduced

EXAMPLE 4

This example demonstrates the catalyst activity for the catalysts of Example 3 for the simultaneous and selective hydrogenation of diolefins and nitriles present in hydrocarbon feedstocks.

The synthetic feedstock set forth Table 2 of Example 2 was processed employing the catalysts of Example 3 under the

same conditions described above in Example 2. The results of each run employing the catalysts of Example 3 are set forth hereinbelow in Table 5.

Table 5

5	Catalyst	% Conversion	%Conversion	%Conversion
		Diolefins	Monoolefins	Nitriles

	6	98	0	21
	7	99	0	82
10	8	0	0	0

As can be seen from Table 5, as was the case with the Group VIII metals discussed above, the concentrations of the active metal phase of the Group IB metals employed have an affect on the selective hydrogenation of the diolefins and nitriles in the hydrocarbon. Copper concentrations as low as 0.80 wt% were effective for the selective and simultaneous hydrogenation of diolefins and nitriles. In addition to the foregoing, the degree of reduction of the metal phase affects the activity of the Group IB metal. However, contrary to the Group VIII metals, the Group IB metals are effective when partially reduced and ineffective when completely reduced. In this regard see Catalyst No. 8 wherein the copper metal phase was completely reduced and no conversation of diolefins, monoolefins or nitriles was accomplished.

EXAMPLE 5

This example demonstrates the importance of the catalyst support on the activity of the catalyst of the present invention.

Carbon granules provided by Johnson Matthey were selected as one catalyst support. A second catalyst support comprising gamma alumina sold by Johnson Matthey under was likewise selected. Both of the supports were impregnated with palladium in the manner described above with regard to Example 1 and the impregnated catalyst supports were then activated by complete reduction at a temperature of 450°C, a pressure of 250 psi for eight hours. Table 6 below sets forth the catalyst composition and activation treatment for each of the two catalysts.

Table 6

Catalyst	Support	Active Metal Phase	Activation
9	gamma alumina	1.0 wt% Pd	completely reduced
10	carbon	0.3 wt% Pd	completely reduced
11	gamma alumina	0.3 wt% Pd	completely reduced

EXAMPLE 6

In order to demonstrate the catalyst activity for the catalysts of Example 5 for the simultaneous and selective hydrogenation of diolefins and nitriles, the synthetic feedstock of Example 2 was treated with the catalysts under the same conditions set forth in Example 2. The results for each run employing the catalysts of Example 5 are set forth below in Table 7.

Table 7

Catalyst	% Conversion Diolefins	%Conversion Monoolefins	%Conversion Nitriles
9	100	88	18
10	100	0	50
11	100	30	20

The carbon supported catalyst, catalyst 10, was effective for the simultaneous hydrogenation of diolefins and nitriles in a selective manner wherein the gamma alumina supported catalysts (9 and 11) achieved no selective conversion of diolefins, monoolefins or nitriles. The results lead one to conclude that carbon and the zeolite present in the inorganic oxide-zeolite composite are effective catalyst supports for the catalysts of the present invention. Both the zeolite and carbon contain moderate Lewis acid sites which are believed to be responsible for

the superior activity characteristics of the catalysts of the present invention.

5 This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are
10 intended to be embraced therein.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A catalyst useful for the simultaneous and selective hydrogenation of diolefins and nitriles present in a hydrocarbon feedstock comprises:

5 (a) a support material selected from the group consisting of an inorganic oxide-zeolite composite, carbon and zeolite; and

10 (b) a catalytically active metal phase selected from the group consisting of partially reduced Group IB metals and completely reduced Group VIII metals, said active metal being present in an amount of about ≥ 0.03 wt%.

2. A catalyst according to claim 1 wherein the support material is an alumina-zeolite composite.

15 3. A catalyst according to claim 2 wherein the surface area of the catalyst is between about 100 to 1500 m^2/g .

4. A catalyst according to claim 2 wherein the surface area of the catalyst is between about 100 to 1000 m^2/g .

5. A catalyst according to claim 2 wherein the surface area of the catalyst is between about 250 to 350 m²/g.

5 6. A catalyst according to claim 2 wherein the pore volume of the catalyst is between about 0.20 cc/g to 1.50 cc/g.

7. A catalyst according to claim 2 wherein the pore volume of the catalyst is between about 0.30 cc/g to 0.70 cc/g.

10 8. A catalyst according to claim 1 wherein the active metal is present in an amount of between about 0.03 to 20 wt%.

9. A catalyst according to claim 1 wherein the active metal is copper.

15 10. A catalyst according to claim 1 wherein the active metal is nickel.

11. A catalyst according to claim 1 wherein the active metal is palladium.

12. A catalyst according to claim 10 wherein the active metal is present in an amount of ≥ 1.00 wt%.

5 13. A method for preparing a catalyst useful for the simultaneous and selective hydrogenation of diolefins and nitriles present in a hydrocarbon feedstock comprises:

10 (a) providing a support material selected from the group consisting of an inorganic oxide-zeolite composite, carbon and zeolite;

 (b) impregnating the support material with a salt of the catalytically active metal phase selected from the group consisting of Group IB metals and Group VIII metals, said active metal being present in an amount of about ≥ 0.03 wt%;

15 (c) drying the impregnated support and calcining the dried impregnated support at a temperature between about 150°C and about 650°C with time sufficient to decompose the metal salt impregnated on the support; and

20 (d) activating the metal phase by at least partial reduction.

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14. A method according to claim 13 wherein the metal phase is a Group IB metal and said activating step comprises temperature (°C) 150-300, Pressure (psi) 15-350, H₂ flow rate (lt/h) 0.1-8.0.

15. A method according to claim 13 wherein the metal phase is a Group VIII metal and said activating step comprises temperature (°C) 200-600, Pressure (psi) 15-150, H₂ flow rate (lt/h) 0.1-8.0.

16. A process for the simultaneous and selective hydrogenation of diolefins and nitriles from a hydrocarbon feedstock comprising:

(a) providing a hydrocarbon feedstock having a diolefin content of ≥ 0.1 wt% and a nitrile content of ≥ 2 ppm(w);

(b) providing a catalyst comprising

1) a support material selected from the group consisting of an inorganic oxide-zeolite composite, carbon and zeolite; and

2) a catalytically active metal phase selected from the group consisting of partially induced Group IB metals and completely reduced Group VIII metals, said active metal being present in an amount of about ≥ 0.03 wt%;

(c) mixing the hydrocarbon feedstock in the presence of the catalyst with hydrogen wherein the ratio of hydrogen to the diolefins and nitriles in the feedstock is less than three times the stoichiometric amount required to selectively hydrogenate the diolefins and nitriles; and

(d) treating the feedstock and hydrogen mixture in the presence of the catalyst at a temperature of about between 50 to 250°C at a pressure of about between 150 to 650 psi.

17. A process according to claim 16 wherein said temperature is between about 60 to 160°C.

18. A process according to claim 17 wherein the pressure is between 200 to 400 psi.

19. A process according to claim 16 wherein the liquid hourly space velocity is in the range of between about 0.1 to 5 h⁻¹.

5 20. A process according to claim 16 wherein the liquid hourly space velocity is in the range of between about 0.5 to 5 h⁻¹.

21. A process according to claim 16 wherein the liquid hourly space velocity is in the range of between about 1 to 4.5 h⁻¹.