

HYDROGENATION OF AROMATIC COMPOUNDS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a process for hydrogenation of aromatic compounds such as the hydrogenation of benzene to cyclohexane and the supported nickel catalyst modified with up to 0.9 wt.% Cu therefor.

Related Information

Cyclohexane is the main precursor for the production of nylon products and as such, the demand remains strong. Cyclohexane was first obtained by the direct fractional distillation of suitable crude petroleum refinery streams. Now the major portion of cyclohexane is obtained from the direct hydrogenation of benzene. Conventionally the reaction is carried out in vapor or mixed phase using a fixed bed reaction. The reactor temperature is controlled to be between 350 to 500°F. Higher temperatures can lead to thermodynamic limitations on benzene conversion, thermal cracking and increased by-product. In general, the amount of byproducts in the effluent stream from a hydrogenation reactor increases with hydrogenation temperature or conversion of benzene or both.

Peterson in U.S. Pat. No. 2,373,501 discloses a liquid phase process for the hydrogenation of benzene to cyclohexane wherein a temperature differential is maintained between the top of the catalyst bed where benzene is fed and the outlet where substantially pure cyclohexane is withdrawn. The temperature differential is due to the change in the exothermic heat of reaction released as less and less benzene is converted as the concentration of benzene decreases. Specifically the top of the catalyst bed is at a higher temperature than the lower catalyst bed. Hydrogen is supplied countercurrent to the benzene/cyclohexane flow. Temperature control coils are disposed within the reactor to maintain the temperature differential if the exothermic heat of reaction is not sufficient or to cool the bed if too much heat is released. Peterson recognizes that although the bulk of his reaction takes place in the liquid phase a portion of the benzene and cyclohexane will be vaporized, especially near the top of the reactor where the benzene concentration is highest and conversion is highest. A reflux condenser is provided to condense the

condensable material and return it to the reactor. Thus, a substantial portion of the heat of reaction is removed by condensation of the reactants vaporized throughout the reaction. Peterson maintains a liquid level above the topmost catalyst bed but allows room for vapors to escape to the condenser where the heat of reaction is removed.

Larkin, et al. in U.S. Pat. No. 5,189,233 disclose another liquid phase process for the hydrogenation of benzene to cyclohexane. However, Larkin, et al utilize high pressure (2500 psig) to maintain the reactants in the liquid state. In addition Larkin, et al disclose the use of progressively more active catalyst as the concentration of benzene decreases to control the temperature and unwanted side reactions.

Hui, et al. in U.S. Pat. No. 4,731,496 disclose a gas phase process for the hydrogenation of benzene to cyclohexane over a specific catalyst. The catalyst reported therein is nickel supported on a mixture of titanium dioxide and zirconium dioxide.

US. Pat. No. 6,750,374 discloses a process for the hydrogenation of benzene using hydrogen containing up to about 15 mole% impurities, such as carbon monoxide and light hydrocarbons with an alumina supported catalyst containing from about 15 to 35 wt.% Ni and from about 1 to 15 wt. % Cu. The catalyst may contain additional elements such as Mo, Zn, Co, Fe.

SUMMARY OF THE INVENTION

The present invention is a process and a catalyst used in the process for hydrogenation of aromatic compounds, such as benzene, aniline, naphthalene, phenol and benzene polycarboxylates, by hydrogenating the aromatic compound in the presence of a catalyst comprising from 4 to 14 wt. % Ni, preferably 9 to 10 wt. % Ni and up to about 0.9 wt. % Cu, preferably about 0.2 to 0.4 wt. % Cu deposited on a transition alumina support having BET surface area of from about 40 to 180 m²/g, and pore volume of from about 0.3 to about 0.8 cc/g. The hydrogenation of aromatic compounds is advantageously carried out in the presence of a high boiling solvent. The preferred solvent will have at least 10° F higher boiling point than the aromatic compound to be hydrogenated and hydrogenated cyclic compound. The advantages of using a high boiling solvent are higher productivity of cyclohexane and keeping the temperature of catalytic reaction zone in a desired range. The high boiling solvent

provides improvement in productivity of the reaction system whether or not the nickel catalyst is modified with copper.

In the production cyclohexane, benzene is present in the reaction stream in an amount of 1 to 60 wt. %, preferentially of 3 to 40 wt.%. The hydrogen stream may be pure hydrogen or may contain up to 5 mole % impurities including carbon monoxide. The remaining components in the reaction stream can be cyclohexane, a high boiling solvent or a mixture of cyclohexane and a high boiling solvent. If a high boiling solvent is used, the solvent may comprise 10 to 90 wt.%, preferably 20 to 80 wt% of the reaction stream. The high boiling solvent may be recovered from the effluent recycle stream and recycled to hydrogenation reactor. The content of cyclohexane in the recycle solvent stream can be 0.0 to 80 wt.%, preferably from 0.5 to 30 wt%.

The present invention also includes a copper modified nickel catalyst used in the hydrogenation of aromatic compound to produce a hydrogenated cyclic compound comprising 4 to 14 wt.% Ni and about 0.2 to 0.4 wt.% Cu deposited on a transition alumina support having BET surface area of from about 40 to 180 m²/g, and pore volume of from about 0.3 to about 0.8 cc/g.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

This invention pertains to a catalytic hydrogenation process of aromatic compounds such as benzene, aniline, naphthalene and phenol in the presence of improved copper modified nickel-based catalyst supported on a porous support. Hydrogenation of benzene yields cyclohexane. But the hydrogenation product stream from the catalytic reactor contains other undesired by-products such as pentane, cyclopentane, methyl cyclopentane, n-hexane and methyl cyclohexane. The product stream usually contains a trace amount of benzene, up to about 200 ppm by weight. Less than 10 ppm benzene is highly desirable for the production of high purity cyclohexane. In general, the amount of by-products in the effluent stream from a hydrogenation reactor increases with hydrogenation temperature or conversion of benzene or both. Especially the amount of the by-products rapidly increases with hydrogenation temperature higher than about 340°F. The hydrogenation of aniline yields cyclohexylamine. But the undesired side reactions are deamination, formation of di and triphenylamine and various heavier products.

An advantage of the present invention is reduced by-products so that simple distillation of hydrogenation product stream produces high purity cyclohexane product. Preferably the cyclohexane product contains no more than about 50 ppm, preferably no more 30 ppm by weight impurities including unconverted benzene excluding impurities came in with the feed benzene. The hydrogenation reactor effluent contains small amounts of cyclohexene. Since cyclohexene can easily be hydrogenated to cyclohexane by recycling the reactor effluent or using a small separate reactor without producing significant amounts of by-product, it is not considered as an undesired by-product. The present invention provides a significant improvement of the productivity of cyclohexane as well as reducing total impurities in the product cyclohexane stream from the catalytic reaction zone to less than 10 ppm, if the benzene hydrogenation is carried out in the presence of a heavy solvent such as decalin and decane. An additional advantage of using heavy solvent is substantially less recycle of hydrogen.

The hydrogenation reaction can be carried out in any physical device such as catalytic distillation column, fixed bed reactor, boiling point reactor, stirred tank reactor, trickle bed reactors or any combination of these. Since the benzene hydrogenation reaction is exothermic reaction, the hydrogenation reaction for the traditional fixed bed operation is preferably carried out by recycling the reactor effluent stream to dilute the fresh benzene feed, which dilutes the heat of reaction. Although recycling the reactor effluent is not necessary for the catalytic distillation reactor, one may choose to do so.

The present catalysts preferably comprise Ni and Cu and optionally one or more elements selected from the group consisting of Ag, Ru, Re, Zn, Mo and Pd which are deposited on a support comprising transitional aluminas such as crystalline alumina of gamma, kappa, delta, theta and alpha or a mixture comprised of two or three selected therefrom. A preferred nickel content of the catalyst is from about 9 to 10 wt.% and a preferred copper contents is from about 0.2 to 0.4 wt.%. The catalyst used in this invention is prepared by depositing nickel and copper on a porous support. Copper serves to improve the catalyst activity and selectivity. The catalyst may contain one or more elements as the second optional modifiers from Ag, Ru, Re, Zn, Mo, and Pd. The deposition of active metal components can be

carried out by any technique such as incipient impregnation, spray coating impregnation. The preferred support will have average of size from about 0.5 mm to about 3 mm, preferably from about 1 mm to about 2.5 mm.

The transition alumina is obtained by calcining at about 850 to about 1200°C, and preferably having the following physical properties after calcining at from 850 to 1200°C: BET surface of from about 40 to about 180 m²/g, preferably from 50 to 120 m²/g and pore volume of from about 0.3 to about 0.8 cc/g.. The transition alumina is the crystalline alumina of delta, theta, kappa or a mixture composed of two or three from gamma, kappa, delta, theta and alpha.

The physical shapes of the preferred aluminas in this invention can be any shape such as spheres, extrudates, pellets and granules which preferably have diameters of less than about 1/4 inch, preferably 1/8 inch and less than about 1/2 inch length, and preferably less than 1/4 inch length for extrudates or pellets.

Deposition of the nickel on a support can be carried out by single or multiple impregnations. A solution of the nickel compound is prepared by dissolving a nickel compound or an organo nickel compound in organic solvent or water. The examples of the nickel compounds are nickel salts such as nickel nitrate or organo metallic nickel compounds such as nickel acetate, nickel formate, nickel acetylacetonate and nickel alkoxides. The impregnation product is dried and calcined at temperature in a range from 200° to 600°C, preferably from 250° to 500°C.

When the hydrogenation of benzene is carried out in a fixed bed reactor, which is operated in boiling point mode, or in a catalytic distillation reactor, the heat of hydrogenation reaction is utilized to vaporize the product cyclohexane. The result of the vaporization is the internal cooling of the hydrogenation reaction zone. The overhead vapor stream from a catalytic distillation reactor, which is operated in the presence or absence of a high boiling solvent, comprises cyclohexane and hydrogen.

Control Example 1

A commercial 28 wt. % Ni catalyst (1.2 mm diameter trilobe extrudates) was tested to hydrogenate of benzene. The crystal form of alumina support of this catalyst is gamma-alumina. The physical properties of this catalyst were 113 m²/g BET, 0.43 cc/g total nitrogen pore volume and an average pore diameter of 15 nm. 50 grams of the catalyst was loaded in a vertically mounted up-flow stainless steel

fixed bed reactor (1 inch diameter x 20 inch long). Two thermocouples at each end of catalyst zone were installed to control the reactor temperature. The catalyst was supplied by the manufacturer as activated and passivated form, and recommended reactivation at 482°F in hydrogen gas flow. The catalyst was reactivated at 250°F in 300 cc/min gas flow of 33 volume % hydrogen gas in nitrogen for 1.5 hours and then 575°F for 5 hours in 350 cc/min flow of pure hydrogen gas. The hydrogenation of benzene was carried out under various conditions. The results are listed in Table 1.

Table 1

Temp °F	300	320	340	340	350	360
Press, psig	250	250	250	250	250	250
Benzene feed rate, ml/min	6	6	11.2	6	6	6
Benzene Conversion, %	18.21	20.21	21.59	17.71	18.41	17.86
Selectivity of cyclohexane and cyclohexene, m%	99.95	99.87	99.91	99.84	99.84	99.82
By-products per 100% cyclohexane and cyclohexene combined, wt. ppm						
Cyclopentane	439	1114	644	1296	1359	1520
Methylcyclohexane	0	0	7	0	0	0
Hexane	0	0	7	0	0	0
Methyl cyclopentane	692	1306	472	1546	1669	1881
Sum of by-products	1131	2420	1130	2842	3028	3401
Cyclohexene	854	165	1661	1201	1309	2056

Example 2

A spherical gamma-alumina (1.68 mm diameter) support was calcined at 1100°C for 3 hours. The alumina spheres prior to the calcination had 145 m²/g BET surface area, a total nitrogen volume of 0.925 cc/g and an average pore diameter of 21.6nm. After calcination, the diameter of alumina spheres was changed to 1.45 mm, which had 56 m²/g BET, a total nitrogen pore volume of 0.701 cc/g and an average pore diameter of 36.2nm. Its x-ray diffraction indicated mostly theta-alumina with minor amount of delta.

A mixed solution of nickel nitrate and copper nitrate was prepared by dissolving 86.5 grams of Ni(NO₃)₂·2.5H₂O in 25.95 grams of water. 300 grams of the calcined alumina was placed in a rotary impregnator. The mixed solution was sprayed on rolling alumina spheres inside the rotary impregnator by using a liquid sprayer over a period of about 15 minutes. The content in the rotary impregnator was dried by blowing hot air in at about 200°C. The dried product was calcined at 350°C for 2 hours.

The second mixed solution was prepared by dissolving 65 grams of Ni(NO₃)₂·6H₂O and 1.8 grams of Cu(NO₃)₂·2.5H₂O in 19.5 grams of water. The second impregnation was performed on the first impregnation product in similar manner to the first impregnation. The dried impregnation product was calcined at 380°C for 2 hours.

Based on the amount of materials used, the finished catalyst would contain 9.22 wt % Ni and 0.35 wt. % Cu. The examination of the catalyst spheres under microscope indicated that the active metal components were deposited in an outer layer of spheres. The average layer thickness was about 0.33 mm. The physical properties of this catalyst were 60 m²/g, 0.56 cc/g total nitrogen pore volume and an average pore diameter of 39 nm. 50 grams of this catalyst was loaded in the same reactor used in the Control Example 1. The catalyst was activated at 250°F in 300 cc/min gas flow of 33 volume % hydrogen gas in nitrogen for 1.5 hours and then for 3 hours at each 670 and 770°F by passing 350 cc/min of pure hydrogen gas. The hydrogenation of benzene was carried out under various conditions. The results are listed in Table 2. As shown in Table 2, the hydrogenation reaction product streams from the reactor do not contain any detectable amounts of by-

products. The performance of this catalyst is superior to the conventional nickel catalysts.

Table 2

Temp °F	300	320	320	340	340	350	360
Press, psig	250	250	250	250	250	250	250
Benzene feed rate, ml/min	6	6	11.2	11.2	6	6	6
Benzene Conversion, %	24.45	18.69	28.28	21.48	25.59	14.34	19.44
Selectivity of cyclohexane and cyclohexene, m%	100	100	100	100	100	100	100
By-products in product stream based on 100% cyclohexane and cyclohexene combined, wt. ppm							
Cyclopentane	0	0	0	0	0	0	0
Methylcyclohexane	0	0	0	0	0	0	0
Hexane	0	0	0	0	0	0	0
Methyl cyclopentane	0	0	0	0	0	0	0
Sum of by-products	0	0	0	0	0	0	0
Cyclohexene	1613	4734	1285	2088	1549	3115	2235

Example 3

A nickel catalyst was prepared according to US Publication No. 2005-0033099-A1. Gamma-Alumina (1.3 mm diameter trilobe extrudates) was calcined at about 1000°C for 3 hours in air. The gamma-alumina had 252 m²/g BET, a total nitrogen pore volume of 0.571 cc/g and an average pore diameter of 8.85 nm. A solution of nickel nitrate was prepared by dissolving 183.6g Ni(NO₃)₂·6H₂O in 295 grams water. 300 g of the calcined alumina support was placed in a rotary impregnator and then the nickel nitrate solution was poured on tumbling alumina extrudates in the rotary impregnator. After 15 minutes cold roll, the content in the rotary impregnator was dried at about 200°C by blowing hot air into the rotary drier. The dried product was calcined at 380°C for 2 hours. Based on the amount of nickel nitrate used to prepare this catalyst, the finished catalyst would have 11 wt % Ni on alumina support. Measurement of the physical properties of the finished catalyst indicated 133 m²/g BET surface area, a total nitrogen pore volume of 0.622 cc/g and an average pore diameter of 18.6 nm.

50 grams of this catalyst was loaded in the same reactor used in the Control Example 1. The catalyst was activated in identical manner to the Example 2. The hydrogenation of benzene was carried out under various conditions. The results are listed in Table 3. Comparing the performance data of this catalyst in Table 3 with those in the Table 1 of the Control Example 1 indicates a superior performance of this catalyst to conventional nickel catalysts, although it was not as good as the catalyst in the Example 2.

Table 3

Temp °F	300	320	340	340	350	360
Press, psig	250	250	250	250	250	250
Benzene feed rate, ml/min	6	6	11.2	6	6	6
Benzene Conversion, %	18.92	28.28	21.48	25.59	14.34	19.44
Selectivity of cyclohexane and cyclohexene, m%	100.00	100.00	99.97	99.94	99.95	99.97

By-products in product
stream based on 100%
cyclohexane and
cyclohexene combined, wt.
ppm

Cyclopentane	0	0	225	493	386	273
Methylcyclohexane	0	0	0	0	0	0
Hexane	0	0	0	0	0	0
Methyl cyclopentane	0	0	0	0	0	0
Sum of by-products	0	0	225	493	386	273
Cyclohexene	555	846	890	565	765	1846

Example 4

This example demonstrates the hydrogenation of benzene with recycle of reactor effluent in the absence of a heavy solvent. But the feed to the reactor comprises fresh benzene feed and reactor effluent stream, which is cyclohexane. This experiment demonstrates hydrogenation of mixed feed stream to hydrogenation, where the mixed feed represents a stream obtained by mixing 1 weight portion of fresh benzene with 3 weight portion of the reactor effluent recycle stream.

The same catalyst (50 grams) in the Example 2 was in the same reactor used in the Control Example 1. The catalyst was activated in same manner to the Example 2. A feed mixture of benzene and cyclohexane was prepared. The composition of the feed was 0.11 wt% lights, 25.41 wt% benzene and 74.48 wt% cyclohexane. The hydrogenation of benzene was carried out under various conditions. The impurities in the feed and product streams were analyzed with a trace gas analysis method. The result is listed in Table 4. The impurities in product streams mostly originated from impurities in the feed. All combined, the total amount of various impurities (listed in Table 4) produced during the hydrogenation of benzene according to this invention is less than 10 ppm. The conversion of benzene could be forced so high that the

benzene contents in the reactor effluent streams could be reduced to less than 35 ppm by weight. This example demonstrates that it is possible to obtain extremely high conversion (>99.99%) of benzene with a cyclohexane selectivity equivalent to about 99.999 mole %. The productivity of cyclohexane at two conditions of the two right columns in Table 4 were 29.2 and 31.8 m/fur per kg catalyst. This is a demonstration of superior catalyst performance compared to the prior art represented by Example 1.

Table 4

Temp-in, °F		144	158	145	160	159	160
Temp-out, °F		299	329	310	300	322	322
Press, psig		230	230	230	230	230	230
H2 Rate, cc/min		155	185	287.5	340	500	500
Flow rate of feed sole, ml/min		6	6	11.2	11.	29.6	10.5
WHSV, hr ⁻¹		5.8	5.8	10.8	10.8	9.2	10.1
Benzene Conversion, %		77.26	99.81	74.21	83.26	100	99.99
Productivity of cyclohexane (m/hr/kg)						29.2	31.8
Trace analysis (wt ppm)	Feed						
Isopentane	1.7	1.2	1.9	0.9	1.0	1.8	1.9
Methylpentane	12.5	12.0	14.3	12.7	13.1	10.9	10.9
Pentane	1.3	1.9	1.6	1.6	1.8	1.7	1.8
Cyclopentane	5.9	8.1	6.4	7.2	7.4	5.8	5.9
Hexane	13.5	13.3	15.3	13.9	14.0	12.4	12.5
Methyl cyclopentane	11.1	12.4	13.1	12.1	12.2	10.8	10.9
Benzene		5.78*	0.05*	6.59*	4.27*	9.9	34.2
Cyclohexane	-	-	-	-	-	-	-
Cyclohexene	4.7	14.8	5.5	24.9	4.8	4.5	0
Methyl cyclohexane	7.2	8.9	7.6	8.7	9.4	9.3	9.4
Toluene	3.1	3.2	3.2	2.3	1.7	0	0

* Weight %

Example 5

This example demonstrates the hydrogenation of benzene in the presence of decalin as high boiling solvent, where the conversions of benzene to cyclohexane are close to 100%.

50 grams of the catalyst prepared in the Example 2 was loaded in the same reactor used in the Control Example 1. The catalyst was activated in same manner to the Example 2. The feed was a mixture of 0.44 wt% lights, 25.26 wt% benzene and 74.30 wt% decalin. The average total combined impurities in the feed, which boil at temperatures near to cyclohexane, was about 14.8 ppm. The hydrogenation of benzene was carried out under various conditions. The impurities in the feeds and product streams were analyzed with a regular gc analysis method and a trace gc analysis method. The results are listed in Table 5. The impurities in products under various conditions were mostly originated from impurities in feed. All combined, the total amount of various impurities produced during the hydrogenation of benzene according to this invention is less than 4 ppm by weight based on 100% cyclohexane. The trace amount of benzene in product stream can be reduced to less than 2 ppm in the product cyclohexane by adjusting the flow rate of hydrogen to the hydrogenation reactor at a given feed rate of benzene.

Surprisingly no trace amount of cyclohexene in any product stream was found. The productivity of cyclohexane was at least 40% higher than carrying out hydrogenation in the absence of a high boiling solvent in Example 4.

Table 5

Temp-in, °F	218	220	219	220
Temp-out, °F	322	330	328	333
Press, psig	230	230	230	230
H2 Rate, cc/min	400	430	385	405
Flow rate of feed sole, ml/min	15	15	13	13
WHSV, hr ⁻¹	16	16	13.9	13.9
Benzene Conversion, %	100	100	100	100
Productivity of cyclohexane (m/hr/kg)	50.9	50.9	44.2	44.3

Trace analysis (wt ppm)	Feed				
Isopentane	1.0	1.4	1.2	1.6	0.3
Pentane	1	0.3	0.3	0.3	0.3
Cyclopentane	0	0.6	0.4	0.3	0.3
Hexane	5.0	0.4	0.3	1.3	1.3
Methyl cyclopentane	1.1	0.6	0.4	0.4	0.4
Benzene	-	14.9	5.1	0.3	0.3
Cyclohexane	-	-	-	-	-
Cyclohexene	0.2	0	0	0	0
Methyl cyclohexane	4.7	7.0	6.7	6.7	6.5
Toluene	2.1	0	0	0	0

Example 6

This example demonstrates the hydrogenation of benzene in the presence of decane as high boiling solvent. The conversions of benzene were so high that the benzene contents in the product streams were close to undetectable.

50 grams of the catalyst prepared in the Example 2 was loaded in the same reactor used in the Control Example 1. The catalyst was activated in same manner to the Example 2. The feed was a mixture of 0.10 wt% lights, 30.26 wt% benzene and 69.64 wt% decane. The average total combined impurities (excluding benzene) in the feed, which boil at temperatures near to cyclohexane, was about 5.77 ppm. The hydrogenation of benzene was carried out under various conditions. The impurities in the feeds and product streams were analyzed with a regular gc analysis method and a trace gc analysis method. The result is listed in Table 6. The impurities in products under various conditions mostly originated from impurities in the feed. All combined, the total amount of various impurities produced during the hydrogenation of benzene according to this invention is about 11 ppm based on 100% cyclohexane. The productivity of cyclohexane was equivalent or better than the case of performing the hydrogenation in the absence of a high boiling solvent in Example 4.

Table 6

Temp-in, ° F		165	165	164
Temp-out, ° F		335	327	334
Press, psig		230	230	230
H2 Rate, cc/min		400	400	450
Flow rate of feed sole, ml/min		9	8.5	10
WHSV, hr ⁻¹		9.6	8	11
Benzene Conversion, %		100	100	100
Productivity of cyclohexane (m/hr/kg)		36.4	32.6	40.5
Trace analysis (wt ppm)	Feed			
Isopentane	0.2	0.2	0.3	0.2
Cyclopentane	0.1	0.9	1.0	0.9
Methyl pentane	<0.1	0.1	0.2	<0.1
Hexane	0.2	0.9	1.0	0.5
Methyl cyclopentane	1.7	2.4	2.4	2.0
Benzene	-	0.02	<0.01	0.02
Cyclohexane	2.5	-	-	-
Cyclohexene	<0.1	1.4	1.3	0
Methyl cyclohexane	2.3	4.6	4.4	4.5
Toluene	1.7	0	0	0

What is claimed is:

1. A copper modified nickel catalyst useful for the hydrogenation of aromatic compound to produce a hydrogenated cyclic compound, the catalyst comprising 4 to 10 wt. % Ni and about 0.2 to 0.9 wt. % Cu deposited on a transition alumina support having a BET surface area from about 40 to 180 m²/g, and a pore volume from about 0.3 to about 0.8 cc/g; and
wherein the catalyst contains one or more modifiers selected from the group consisting of Ag and Ru.
2. The catalyst according to claim 1 wherein the catalyst further contains one or more modifiers selected from the group consisting of Re, Zn, Mo and Pd.
3. The catalyst according to claim 1 wherein the Cu content is about 0.2 to 0.4 wt. %.
4. The catalyst according to claim 1 wherein the Ni content of the catalyst is about 9 to 10 wt. %.
5. The catalyst according to claim 1:
wherein the Ni content of the catalyst is about 9 to 10 wt. %;
wherein the Cu content is about 0.2 to 0.4 wt. %; and
wherein the catalyst further contains one or more modifiers selected from the group consisting of Re, Zn, Mo and Pd.
6. The catalyst according to claim 1, wherein the transition alumina support is obtained by calcining at a temperature in the range from about 850 to about 1200°C.
7. The catalyst according to claim 1, wherein the transition alumina support has a BET surface area from about 50 to about 120 m²/g.
8. The catalyst according to claim 1, wherein the transition alumina comprises one or more of delta alumina, theta alumina, and kappa alumina.
9. A copper modified nickel catalyst useful for the hydrogenation of benzene to produce cyclohexane, the catalyst comprising

4 to 10 wt. % Ni and about 0.2 to 0.9 wt. % Cu deposited on a transition alumina support having a BET surface area from about 40 to 180 m²/g and a pore volume from about 0.3 to about 0.8 cc/g; and

wherein the catalyst contains one or more modifiers selected from the group consisting of Ag and Ru.

10. The catalyst according to claim 9 wherein the catalyst further contains one or more modifiers selected from the group consisting of Re, Zn, Mo and Pd.

11. The catalyst according to claim 9 wherein the Cu content is about 0.2 to 0.4 wt. %.

12. The catalyst according to claim 9 wherein the Ni content of the catalyst is about 9 to 10 wt. %.

13. The catalyst according to claim 9:
wherein the Ni content of the catalyst is about 9 to 10 wt. %;
wherein the Cu content is about 0.2 to 0.4 wt. %; and
wherein the catalyst further contains one or more modifiers selected from the group consisting of Re, Zn, Mo and Pd.

14. The catalyst according to claim 9, wherein the transition alumina support is obtained by calcining at a temperature in the range from about 850 to about 1200°C.

15. The catalyst according to claim 9, wherein the transition alumina support has a BET surface area from about 50 to about 120 m²/g.

16. The catalyst according to claim 9, wherein the transition alumina comprises one or more of delta alumina, theta alumina, and kappa alumina.