

[72] Inventors **Stephen M. Kovach;**
Ronald A. Kmecak, both of Ashland, Ky.
 [21] Appl. No. **785,248**
 [22] Filed **Dec. 19, 1968**
 [45] Patented **Sept. 21, 1971**
 [73] Assignee **Ashland Oil & Refining Company**
Houston, Tex.

Primary Examiner—Delbert E. Gantz
Assistant Examiner—G. E. Schmitkons
Attorney—Walter H. Schneider

[54] **ALKYL TRANSFER OF ALKYL AROMATICS**
WITH GROUP VIII METALS ON BORIA-ALUMINA
17 Claims, 1 Drawing Fig.

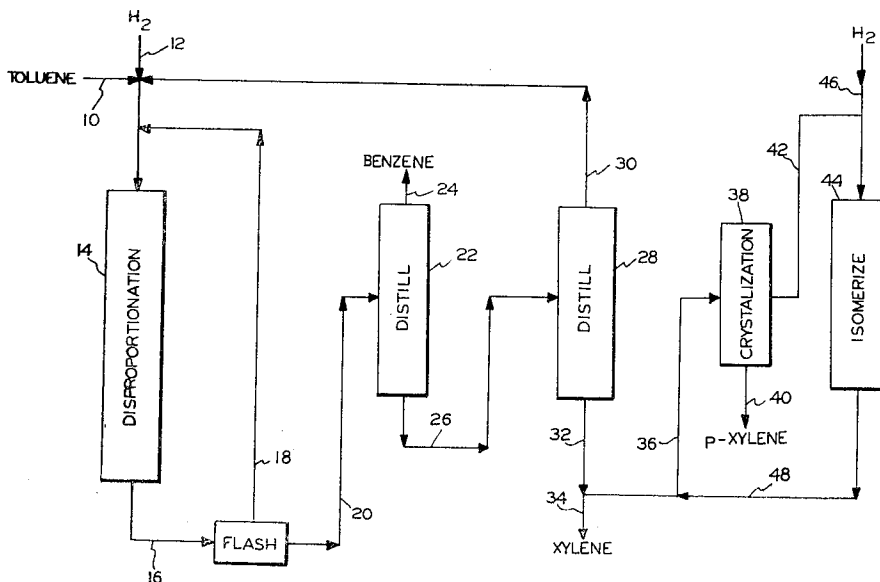
[52] U.S. Cl. **260/672 R,**
252/462, 252/466, 260/668 A, 260/672 T,
260/674 A
 [51] Int. Cl. **C07c 3/58,**
C07c 15/08, B01j 11/06
 [50] Field of Search **260/672 T**

[56] **References Cited**

UNITED STATES PATENTS

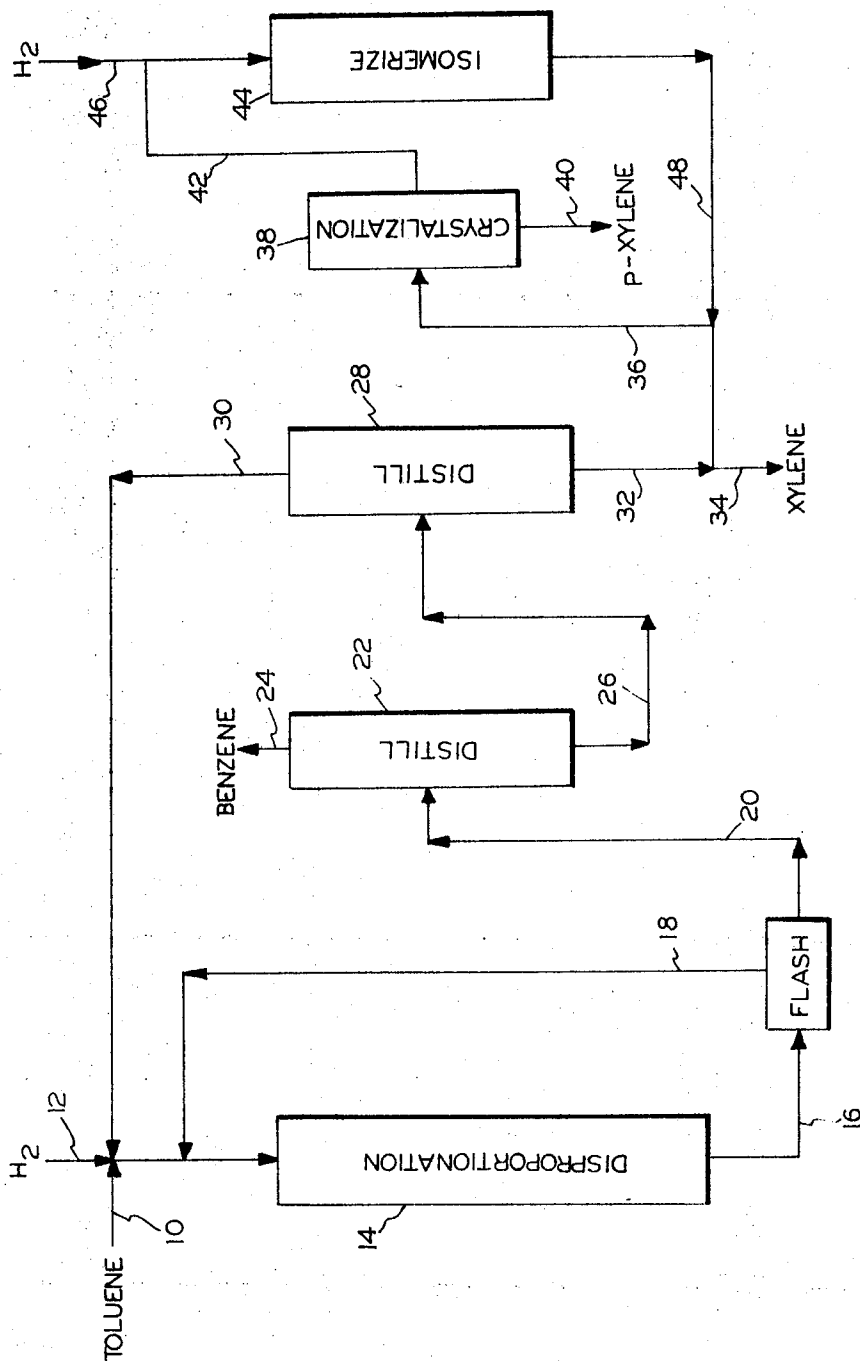
2,795,629	6/1957	Boedeker	260/668
3,079,447	2/1963	Bartlett et al.	260/668
3,113,979	12/1963	Bartlett et al.	260/668

ABSTRACT: A process for the alkyl transfer of alkyl aromatics including contacting an alkyl aromatic feed material, such as toluene, with a catalyst comprising a Group VIII metal, such as nickel, platinum, or palladium and boria deposited on an alumina base at a temperature of about 800° to 1100° F., a pressure of about 0 to 2000 p.s.i.g., and a liquid hourly space velocity of about 0.1 to 10, and in the presence of hydrogen introduced at a rate of about 1 to 10 moles hydrogen per mole of hydrocarbon feed. Promoters selected from Group I, Group II, Group IV, and the Rare Earth metals of the Periodic System may be added to the catalyst. Deactivated catalyst may be periodically rejuvenated by discontinuing the introduction of aromatic feed material and purging with hydrogen and the catalyst can be reactivated by calcination in an atmosphere such as air. Where toluene is the feed, the alkyl transfer product may be distilled to separate benzene, toluene and xylenes, the toluene may be recycled to the alkyl transfer step, the xylenes may be crystallized to separate para-xylene from the remaining xylenes, the mother liquor from the crystallization step may thereafter be isomerized to readjust the para-xylene content and the product of the isomerization may be recycled to the crystallization zone.



PATENTED SEP 21 1971

3,607,961



INVENTOR
Stephen M. Kovach
Ronald A. Kmesak
BY Walter H. Schneider
ATTORNEY

ALKYL TRANSFER OF ALKYL AROMATICS WITH GROUP VIII METALS ON BORIA-ALUMINA

BACKGROUND OF THE INVENTION

The present invention relates to a process for the catalytic conversion of hydrocarbons and, more particularly, to a process for the catalytic alkyl transfer of alkyl aromatics.

Aromatic hydrocarbons, such as benzene, naphthalene, and their alkyl derivatives are important building blocks in the chemical and petrochemical industries. For example, benzene and its derivatives have numerous uses; cyclohexane is utilized in nylon production; naphthalene is utilized in the production of phthalic anhydride for alkyd resins, etc., paraxylene can be used for the production of terephthalic acid which, in turn, is utilized in the production of synthetic resins, such as dacron, mylar, etc., etc.

For many years, the primary source of such aromatic hydrocarbons has been coal tar oils obtained by the pyrolysis of coal to produce coke. Such coal tar oils contain principally benzene, toluene, naphthalene, methylnaphthalene and paraxylene. Benzene may be produced from such oils by direct separation, such as distillation techniques, the paraxylene may be separated by crystallization, and the naphthalene fractions by direct separation techniques. Further alkyl derivatives of benzene and naphthalene can be converted to increased volumes of benzene and naphthalene by hydrodealkylation. More recently, however, the petroleum industry has become a leading source of these aromatic hydrocarbons. The reason for this has been the availability of the catalytic reforming process in which naphthene hydrocarbons are dehydrogenated to produce a reformat rich in aromatics and more efficient processes for separating the aromatics from the reformat.

Some years ago, there was a high demand for toluene which was used in the production of TNT. This led to the building of substantial facilities for its production. However, the advent of nuclear and fusion weaponry and the use of diesel oil-ammonium nitrate explosives has left toluene in substantial oversupply, since the only major uses of toluene are as a solvent, the production of toluene diisocyanates and the production of benzene. This has resulted in extensive efforts to develop methods for converting toluene to benzene. One method of converting toluene to benzene is by the previously mentioned hydrodealkylation.

Dealkylation has the primary disadvantage that methane is a major product. Volume yields of benzene are therefore low and carbon deposition on the catalyst is high. The large amounts of methane, while useful as a fuel, require expensive techniques for the removal of the methane from the circulating hydrogen stream utilized in the hydrodealkylation. In addition, large quantities of hydrogen are consumed in the dealkylation process and hydrogen is often in short supply and expensive to produce. Finally, where catalysts are used in the process, carbon laydown on the catalyst is a serious problem.

A more profitable reaction for changing alkyl aromatics to other aromatic products is an alkyl transfer reaction. An alkyl transfer reaction is a process wherein alkyl groups are caused to be transferred from the nuclear carbon atoms of one aromatic molecule to the nuclear carbon atoms of another aromatic molecule. By way of example, an aromatic hydrocarbon molecule containing one nuclear alkyl substituent, such as toluene, may be treated by disproportionation to produce an aromatic hydrocarbon with no alkyl substituents, namely, benzene, and aromatic hydrocarbon molecules with two nuclear alkyl substituents, namely, benzene, and aromatic hydrocarbon molecules with two nuclear alkyl substituents, namely xylenes. Similarly, product ratios may be shifted by transalkylation of xylene and benzene to toluene. Such an alkyl transfer reaction has distinct advantages: methane is not produced in addition to the desired aromatic hydrocarbon. As a result, there is very little loss of product in alkyl transfer as opposed to hydrodealkylation.

Alkyl transfers may be carried out thermally. However, thermal alkyl transfer results in demethylation due to cracking and hydrogenation, ultimately resulting in low yields of desired aromatics. On the other hand, catalytic alkyl transfer has not been highly successful since it requires an active, rugged, acidic catalyst. Typical catalysts are solid oxides, such as silica-alumina, silica-magnesium, etc. These materials, however, are not active enough to promote disproportionation at high conversion rates. In addition, as is the case in hydrodealkylation, carbon deposition on the catalyst and its affect on catalyst activity with time is a severe problem.

It is therefore an object of the present invention to provide an improved process for the conversion of alkyl aromatics. Another object of the present invention is to provide an improved process for the alkyl transfer of alkyl aromatics. Yet another object of the present invention is to provide an improved process for the disproportionation of toluene to produce benzene and xylenes. Another and further object of the present invention is to provide an improved process for the disproportionation of alkyl aromatics which utilizes a novel catalyst system. Another object of the present invention is to provide an improved process for the disproportionation of alkyl aromatics with a catalyst system resistant to carbon laydown. A further object of the present invention is to provide an improved process for the catalytic disproportionation of alkyl aromatics utilizing a Group VIII metal and boria on an alumina base. A further object of the present invention is to provide an improved process for the disproportionation of alkyl aromatics utilizing critical conditions of temperature and pressure which produce maximum disproportionation and conversion of one aromatic to another. Still another object of the present invention is to provide an improved process for the conversion of toluene to benzene and xylenes and conversion of meta- and ortho- xylenes to additional para-xylene. These and other objects and advantages of the present invention will be apparent from the following detailed description.

SUMMARY OF THE INVENTION

Briefly, in accordance with the present invention, alkyl transfer of alkyl aromatics comprises contacting an alkyl aromatic feed material with a catalyst comprising a metal of Group VIII of the Periodic System and boria deposited on an alumina base. Further improvement of the catalyst is obtained by adding a Group I, Group II, Group IV, a Rare Earth metal or mixtures thereof. Further improvements of the process are obtained by maintaining the temperature between about 800 and 1100° F and the pressure between about 0 and 2000 p.s.i.g. Where toluene is the feed, additional para-xylene is produced by isomerizing ortho- and meta- xylenes.

BRIEF DESCRIPTION OF THE DRAWINGS

The drawing shows a flow diagram of the process system in accordance with the present invention

DETAILED DESCRIPTION OF THE INVENTION

Alkyl aromatic feed materials for use in accordance with the present invention can be any alkyl aromatic having at least one transferrable alkyl group. Primary materials are alkyl aromatics having from 7 to 15 carbon atoms, mixtures of such alkyl aromatic hydrocarbons, or hydrocarbon fractions rich in such alkyl aromatic hydrocarbons. Such feeds include mono- and di- aromatics, such as alkyl benzenes and alkyl naphthalenes. Preferably, the alkyl group should contain no more than about 4 carbon atoms. A preferred feed in accordance with the present invention is toluene. Accordingly, disproportionation of toluene will be referred to hereinafter in the detailed description.

The process of the present invention should be conducted at a temperature between about 800 and 1100° F., and preferably between 850 and 1000° F. It has been found in accordance with the present invention that below this temperature range, substantially decreased conversion occurs due to hydrogenation. On the other hand, when operating above this

temperature range, thermal demethylation occurs. The pressure utilized in accordance with the present invention has also been determined to be a critical factor. Accordingly, the process should be carried out between about 0 and 2000 p.s.i.g. and preferably, between 300 to 600 p.s.i.g. It has been found that below the desired pressure range, conversion is low and the aromaticity of the product is high. On the other hand, at higher pressures, conversion is high, but liquid recoveries are low due to hydrogenation and hydrocracking. A liquid hourly space velocity between about 0.1 and 10, and preferably between 0.25 and 1.0, should be utilized and a hydrogen-to-hydrocarbon mole ratio between about 1 and 10 to 1 and preferably between 2 and 4 to 1 is desired.

The high severity conditions required to obtain disproportionation of alkyl aromatics, particularly the disproportionation of toluene, has been found to lead to catalyst deactivation due to selective adsorption and condensation of aromatics on the catalyst surface and carbon laydown on the catalyst. It was found that the condensation and adsorption of aromatics on the catalyst is a temporary poison and that this condition can be alleviated by utilizing high hydrogen partial pressures. In addition, this temporary deactivation of the catalyst can be overcome to completely rejuvenate the catalyst to near virgin activity by hydrogen-purging of the catalyst in the absence of aromatic hydrocarbon feed. While coke or carbon deposition on the catalyst is a permanent poison, it has been found, in accordance with the present invention, that carbon laydown can be decreased by utilizing the catalysts of the present invention. Further, it was found that when these catalysts become deactivated by carbon laydown, they can be restored to near virgin activity by regeneration in air.

The catalyst employed in accordance with the present invention is a multifaceted cure for many of the ills of catalytic disproportionation reactions. First, it has been found that boria deposited on an alumina base is vastly superior to a silica-alumina base catalyst; the former consistently proving to be twice as active as the latter. The amount of boria deposited on the alumina may vary between about 5 and 25 percent by weight of the finished catalyst. The alumina is preferably a gamma alumina. Such gamma aluminas are very stable up to temperatures of about 1800° F. One such alumina, Boehmite, may be prepared in a variety of ways, one of the simplest being the addition of ammonium hydroxide to a water solution of aluminum chloride. The material originally precipitated is an amorphous alumina flock which rapidly grows to crystal size yielding crystalline Boehmite. Aging of Boehmite in ammonium hydroxide solution transforms the Boehmite first to the meta-stable Bayerite and finally to the highly stable Gibbsite. The Bayerite is preferred any may be in its beta- or eta-form.

The active Group VIII metal added to the boria-alumina may be broken down into two families; namely, the ferrous or first transition series, such as nickel and cobalt, and the precious metals or second and third transition series, such as platinum, palladium, rhodium, ruthenium, etc. A ferrous group metal should be present on the finished catalyst in amounts between about 0.5 and 5 percent by weight while a precious metal component should be present in amounts between about 0.01 and 1 percent by weight.

It has also been found that conversion may be improved and, more significantly, carbon laydown on the catalyst may be reduced by the addition thereto of a promoter. Such promoters may be selected from Group I of the Periodic System, such as potassium, rubidium, cesium, etc., Group II of the Periodic System, such as calcium, magnesium, strontium, etc., a Rare Earth metal of the Periodic System, such as cerium, thorium, etc., a Group IV metal of the Periodic System, such as tin or lead, or mixtures of these, and particularly mixtures of a Group IV metal with one of the other groups mentioned. The promoters are preferably in their oxide form and are present in amounts of about 1 to 15 percent by weight based on the weight based on the weight of the finished catalyst.

The catalysts may be prepared by techniques well known in the art. For example, such preparation may include coprecipitation or impregnation techniques. One can employ extrudates or pellets for impregnation or powders followed by pelletization or extrusion to yield the finished catalyst. When employing impregnation techniques, the metals may be added to the base singly or in combination, utilizing water soluble salts such as borates, boric acid, halides, nitrates, sulfates, acetates, etc. Easily hydrolyzed salts can be kept in solution without decomposition by employing the appropriate inorganic acids. Well-known procedures for drying and calcination of the catalyst will also be employed. For example, vacuum drying at a temperature of about 250° F and calcination in an oxidative, neutral or reductive atmosphere, utilizing a calcination temperature of about 800 to 1200° F can be practiced.

Preparation of a specific catalyst is illustrated below. To 200 ml. of distilled water was added 18 grams of nickel nitrate, hexahydrate and 42 grams of boric acid. The solution was heated until all the metal salts went into solution. This hot solution was added slowly to 250 mls. of Bayerite alumina and allowed to stand for 15 minutes. At the end of this period, the liquid was decanted from the impregnated alumina. The resulting catalyst was dried at 250° F for one hour in a vacuum oven and then calcined in a muffle furnace at 950° F in air for 8 hours. The resultant catalyst contained 1 percent nickel oxide, 10 percent boria and the remainder alumina.

The following table shows the results of the treatment of toluene in accordance with the present invention utilizing three of the catalysts contemplated herein.

TABLE I

Catalyst	Catalyst		
	0.3% Pt, 10% B ₂ O ₃ -Al ₂ O ₃	0.1% Pd, 10% B ₂ O ₃ -Al ₂ O ₃	1.0% Ni, 10% B ₂ O ₃ -Al ₂ O ₃
Temp., ° F	1,000	1,000	1,000
Pressure, p.s.i.g.	400	400	400
LHSV	1	1	1
H ₂ /C, m./m	3	3	3
Conversion, wt. percent feed	36	27	21
Δ conversion wt. percent per hr	5	3	0.9
Liquid recovery	88	93	95
Selectivity	88	93	96

It will be seen from the preceding Table that all of the catalysts are highly effective in the conversion of toluene to benzene and xylenes. However, the precious metals have one disadvantage in this process, namely, rather high hydrogenation activity which results in the production of naphthalenes and cracked products. On the other hand, while nickel from the ferrous metal group gives a lower conversion, liquid recoveries are much higher than those obtained with the precious metal catalysts. Hence, the catalysts of the precious metal group are superior. It has also been found that keeping the ferrous metal group metal between about 1 and 4 percent is highly desirable. At 1 percent this catalyst gives a high selectivity whereas, at 4 percent this catalyst is approximately equivalent to the precious metal group catalysts. It has also been found that when utilizing the precious metal catalysts, process conditions should be maintained within the narrower limits specified. Hence, the temperature should be between about 925 and 1000° F, the pressure between about 300 and 600 p.s.i.g. a liquid hourly space velocity between 0.25 and 1, and hydrogen-to-hydrocarbon mole ratio between 1 and 3 to 1.

The improvements obtained by adding a promoter to either a precious metal or a first transition metal catalyst is illustrated by Table II;

TABLE II

	Catalyst	
	0.6 Pd-2SnO ₃ , 10% B ₂ O ₃ -Al ₂ O ₃	1 Ni-2SnO ₃ , 10% B ₂ O ₃ -Al ₂ O ₃
Feed.....	Toluene	
Conditions:		
Temp., ° F.....	1,000	1,000
Pressure, p.s.i.g.....	800	800
LHSV.....	0.5	0.5
H ₂ /H ₂ C.....	3/1	3/1
Recovery, vol. percent.....	88	86
Toluene conversion.....	41.5	48.3
Product distribution:		
< Benzene.....	1.4	2.0
Benzene.....	24.2	28.3
Toluene.....	66.5	60.1
Xylene.....	7.2	9.4
> Xylene.....	0.7	0.2
Carbon on catalyst, wt. percent feed.....	1.55	2.0

It is to be observed from the above that the severity of operation can be increased without penalizing conversion or carbon laydown on the catalyst.

In accordance with the present invention, an integrated process for the production of benzene and paraxylene from toluene can be carried out with resultant high yields of these two valuable products. This process is best described by reference to the drawing.

In accordance with the drawing, toluene is introduced to the system through line 10, hydrogen is added through line 12 and these materials are passed over the catalyst of the present invention in the disproportionation reactor 14. The effluent passing through line 16 is passed to a flash drum for the removal of hydrogen and any light gases produced. These materials are discharged through line 18. Since little or no demethanation occurs, the hydrogen is substantially pure and may be recycled to the disproportionation reaction without further treatment. However, in some instances, further purification of the hydrogen is necessary before recycle or reuse. The liquid product passes through line 20 to a first distillation unit 22. In distillation unit 22, benzene is recovered as an overhead through line 24. The bottoms product from distillation unit 22 passes through line 26 to a second distillation unit 28. In distillation unit 28, toluene is removed as an overhead product and recycled to the disproportionation section through line 30. The bottoms product from distillation unit 28 is a mixture of xylenes which is discharged through line 32. This product may be withdrawn, as such, through line 34. Preferably, however, the xylene product is passed through line 36 to crystallization unit 38. In crystallization unit 38, paraxylene is selectively removed and withdrawn through line 40. The mother liquor from the crystallization section is passed through line 42 to an isomerization unit 44. Hydrogen is added through line 46. In the isomerization unit 44, the equilibrium concentration of paraxylene is reestablished and the material may then be recycled through line 48 to crystallization unit 38 for further paraxylene separation.

The isomerization reaction should be carried out under more mild conditions than the disproportionation. Catalysts useful in the disproportionation reaction might also be used in the isomerization or conventional catalysts, such as, platinum on silica-alumina, can be used. The isomerization may be carried out at temperatures of about 500 to 900° F, and preferably 550 to 650° F, pressures of 50 to 2000 p.s.i.g., and preferably 300 to 600 p.s.i.g., at a liquid hourly space velocity of 0.1 to 10, and utilizing a hydrogen-to-hydrocarbon mole ratio between about 1 and 20 to 1.

When reference is made herein to the Periodic System of Elements, the particular groupings referred to are as set forth in the Periodic Chart of the Elements in "The Merck Index," Seventh Edition, Merck & Co., Inc., 1960.

The term "alkyl transfer" of alkyl aromatics as used herein is meant to include disproportionation and transalkylation. Disproportionation, in turn, is meant to include conversion of two moles of a single aromatic, such as toluene, to one mole each of two different aromatics, such as xylenes and benzene. Transalkylation is meant to include conversion of one mole each of two different aromatics, such as xylenes and benzene, to one mole of a single different aromatic, such as toluene. The alkyl transfer defined above is also to be distinguished

from isomerization where there is no transfer of alkyl groups from one molecule to another but simply a shifting of alkyl group around the aromatic ring, such as isomerization of xylenes, or rupture of the rings or the alkyl side chain and rearrangement of slip-off carbon atoms on the same molecule. The alkyl transfer is also to be distinguished from a hydrogen transfer reaction, such as the hydrogenation of aromatics, the dehydrogenation of cyclo-paraffins and like reactions.

We claim:

1. A process for the alkyl transfer of alkyl aromatics; comprising, contacting an alkyl aromatic feed material with a catalyst comprising about 0.01 to 5 percent by weight of a Group VIII metal of the Periodic System and about 5 to 25 percent by weight of boria and a promoting amount of 1-15 percent by weight of a metal selected from the group consisting of Group I, Group II, Group IV, and the Rare Earth metals of the Periodic System and mixtures thereof deposited on an alumina base, under conditions sufficient to cause alkyl transfer of said alkyl aromatics including a temperature of about 800 to 1100° F.

2. A process in accordance with claim 1 wherein the Group VIII metal is a metal of the first transition series of Group VIII.

3. A process in accordance with claim 1 wherein the metal is nickel.

4. A process in accordance with claim 1 wherein the Group VIII metal is a precious metal.

5. A process in accordance with claim 1 wherein the feed material contains substantial volumes of toluene.

6. A process in accordance with claim 5 wherein unconverted toluene is separated from the alkyl transfer product and said unconverted toluene is recycled to the disproportionation step.

7. A process in accordance with claim 5 wherein xylenes are separated from the alkyl transfer product and paraxylene is separated from said xylenes.

8. A process in accordance with claim 7 wherein the xylenes remaining after the separation of paraxylene are subjected to isomerization conditions sufficient to produce additional paraxylene.

9. A process in accordance with claim 1 wherein the flow of feed material through the catalyst is interrupted periodically and the flow of hydrogen is continued for a time sufficient to reactivate the catalyst.

10. A process in accordance with claim 1 wherein the flow of feed material and hydrogen through the catalyst is discontinued and the catalyst is calcined in air under conditions sufficient to reactivate the catalyst.

11. A process for the alkyl transfer of alkyl aromatics; comprising, contacting an alkyl aromatic feed with a catalyst comprising about 0.01 to 5 percent by weight of a metal of the first transition series of Group VIII of the Periodic System and about 5 to 25 percent by weight of boria deposited on an alumina base, under conditions sufficient to cause alkyl transfer of said alkyl aromatics including a temperature of about 800 to 1100° F., a pressure of about 0 to 2000 p.s.i.g., a liquid hourly space velocity of about 0.1 to 10, and hydrogen to hydrocarbon mol ratio between about 1 and 10 to 1.

12. A process in accordance with claim 11 wherein the feed material contains substantial volumes of toluene.

13. A process in accordance with claim 12 wherein unconverted toluene is recycled to the disproportionation step.

14. A process in accordance with claim 12 wherein xylenes are separated from the alkyl transfer product and paraxylene is separated from said xylenes.

15. A process in accordance with claim 14 wherein the xylenes remaining after the separation of paraxylene are subjected to isomerization conditions sufficient to produce additional paraxylene.

16. A process in accordance with claim 11 wherein the flow of feed material through the catalyst is interrupted periodically and the flow of hydrogen is continued for a time sufficient to reactivate the catalysts.

17. A process in accordance with claim 11 wherein the flow of feed material and hydrogen through the catalyst is discontinued and the catalyst is calcined in air under conditions sufficient to reactivate the catalyst.