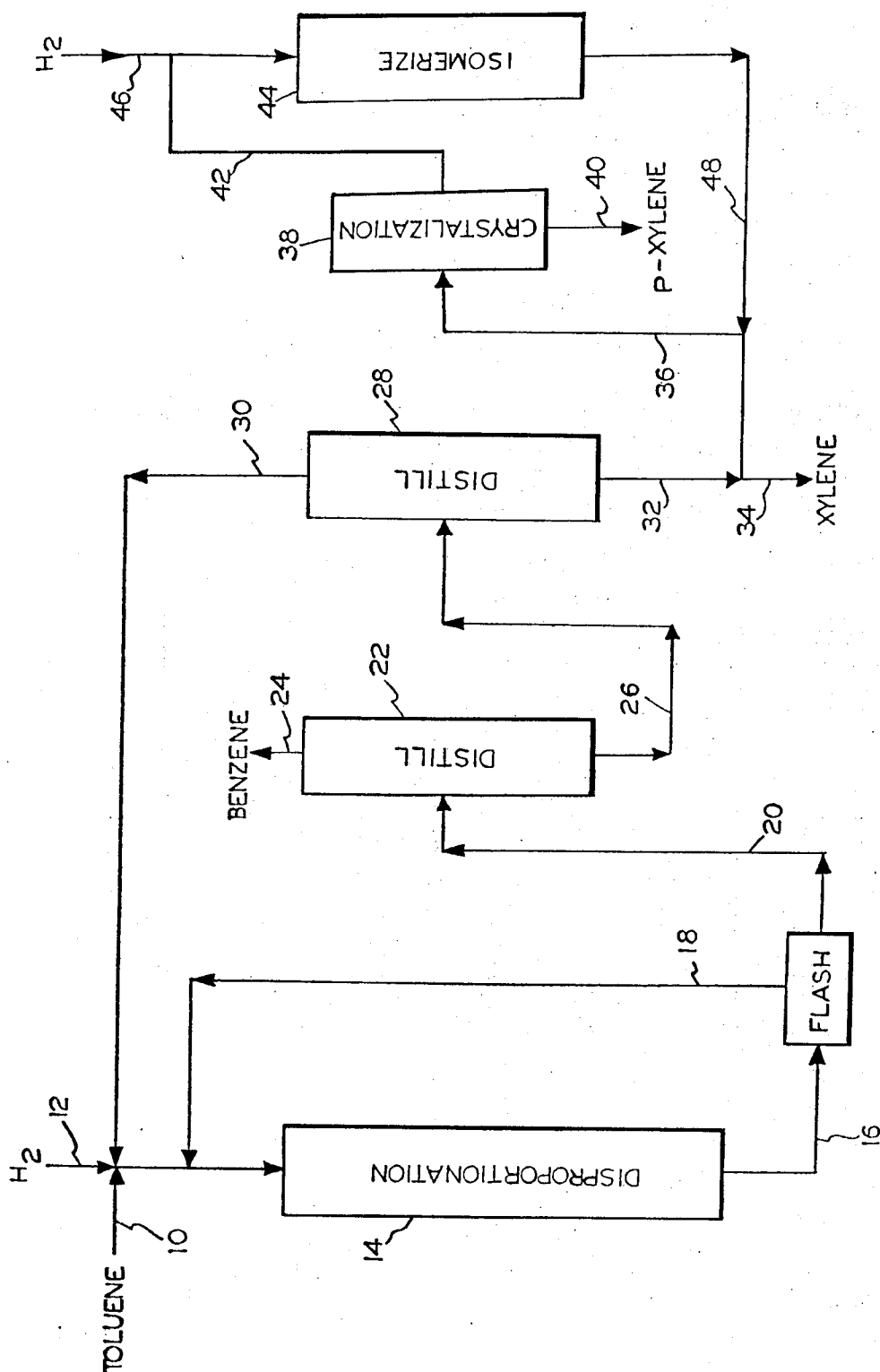


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 OR VANADIUM AND MANGANESE AND TIN
 METALS ON MORDENITE
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ALKYL TRANSFER OF ALKYL AROMATICS WITH CHROMIUM OR VANADIUM AND MANGANESE AND TIN METALS ON MORDENITE

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ABSTRACT OF THE DISCLOSURE

Alkyl transfer, such as disproportionation, of alkyl aromatics is accomplished by contacting an alkyl aromatic feed material with a catalyst comprising chromium or vanadium and promoter consisting of a mixture of tin and manganese all supported on a synthetic mordenite.

NATURE OF INVENTION

The present invention relates to a process for the catalyst alkyl transfer of alkyl aromatics.

BACKGROUND OF THE INVENTION

Aromatic hydrocarbons, such as benzene, naphthalene, and their alkyl derivatives, are important building blocks in the chemical and petroleum 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 alkyl resins, etc.; para-xylene 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.

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 an alkyl transfer reaction (disproportionation) to produce an aromatic hydrocarbon with no 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. Our co-pending U.S. applications, Ser. No. 785,177, now U.S. Pat. No. 3,699,181, and Ser. No. 785,251, both filed on Dec. 19, 1968, discuss the advantages and desirabilities of processes for alkyl transfer utilizing metals such as platinum, palladium, ruthenium, rhodium, chromium, molybdenum, and tungsten on a suitable oxide support such as mordenite or other synthetic zeolites. Those two applications also disclose the use of promoter metals such as tin and lead.

An object of the present invention is to provide an improved process for the alkyl transfer of alkyl aromatics. Another object of the present invention is to provide an improved process for the disproportionation of toluene to produce benzene and xylenes. Another object of the present invention is to provide an improved process for the disproportionation of alkyl aromatics which utilizes a novel catalyst system. 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

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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 is accomplished by contacting an alkyl aromatic feed material with a catalyst comprising a metal selected from the group consisting of chromium and vanadium deposited with both manganese and tin on a synthetic mordenite base. Further improvements of the process are obtained by maintaining the temperature between about 700 and 1050° 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 transferable 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, a disproportionation of toluene will be referred to hereinafter in the detailed description.

The process of the invention should be conducted at a temperature between about 700 and 1050° F., and preferably between about 800 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 200 to 1000 p.s.i.g. It has been found that below the desired pressure range, conversion is low and 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 0.5 and 2 should be utilized and a hydrogen to hydrocarbon mol ratio between 1 and 10 to 1 and preferably 0.5 and 2 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 in 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 zeolites are a class of hydrated silicates of aluminum and either sodium or calcium or both, having the general formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot x\text{H}_2\text{O}$. Originally, the term zeolite described a group of naturally-occurring minerals which were principally sodium or calcium aluminosilicates. Such naturally-occurring zeolites include, for example, chabazite, gmelinite, crionite, faujasite, analcite, heulandite, natrolite, stilbite, thomsonite, etc. Synthetic zeolites are generally known on the trade by a trade name or a trade designation applied by the specific manufacturer. For example, Types A, X and Y are manufactured by Linde Company and a synthetic mordenite is designated Zeolon by its manufacturer, the Norton Company. Zeolites generally have a rigid, three-dimensional anionic network with intracrystalline channels whose narrowest cross-section has essentially a uniform diameter. Thus, zeolites of both natural and synthetic origin, can be distinguished from crystalline aluminosilicate clays, such as bentonite, which have a two-dimensional layer structure, and silica-alumina synthetic catalysts which are amorphous aluminosilicates having a random structure.

Zeolites whose atoms are arranged in crystal lattices in such a way that there are a large number of small cavities interconnected by smaller openings or pores of precisely uniform size are generally referred to as molecular sieves. Some natural zeolites exhibit molecular sieve characteristics to a limited degree. However, the synthetic zeolites as a class exhibit these characteristics.

A synthetic zeolite found particularly effective in the present process is a Type Y molecular sieve manufactured by Linde Company. This material has the general formula $\text{Na}_{56+y}[(\text{AlO}_2)_{56+y}(\text{SiO}_2)_{136-y}]$ where y has a value of about 0 and can vary from -8 to 20. The Type Y zeolite crystallizes in the cubic system and the lattice constant for the sodium form, with a Si/Al ratio of 2.5, is 24.66 Å. In the sodium form of Y, the negative charge in each AlO_4 is balanced by a closely associated sodium atom. In the divalent cationic form, however, the divalent cation, usually calcium or magnesium, is asymmetrically located with respect to the aluminas.

Synthetic mordenite, designated Zeolon by the Norton Company, has a high silicon to aluminum ratio, generally about 5 to 1. The postulated formula for this material is $(\text{Ca}, \text{Na}_2)\text{Al}_2\text{Si}_6\text{O}_{22} \cdot 6\text{H}_2\text{O}$. The basic unit is a tetrahedron consisting of one silicon or aluminum atom surrounded by 4 oxygens. The crystal is made up of 4 and 5-membered rings of these tetrahedra. The chains are linked together to form a network having a system of large parallel channels interconnected by small cross channels.

The active metal added to the zeolite is one selected from the group consisting of chromium and vanadium. Processes for depositing chromium or vanadium (the active metal) and the promoter mixture of manganese and tin metals of the present invention on the zeolites are well known in the art. This simply consists of replacing all or a part of the exchangeable cations of the zeolite with the metallic ions by ion exchange. The chromium or vanadium should be present in amounts between about 0.5 and 20% by weight.

The Type Y or the mordenite may be utilized in accordance with the present invention by first converting

the sodium or calcium form to the hydrogen form which is often referred to as the acid form. Conversion to the hydrogen form may be carried out by either replacement of the metal cations with hydrogen ions or by replacement of the metal ions with ammonium ions, followed by the decomposition of the ammonium by calcination. By this technique, from 95 to 99% of the metal is removed and replaced by hydrogen. Thereafter, the desired active metal, copper or chromium, is exchanged for the hydrogen to form the finished catalytic material.

It has been found that the conversion may be improved and, more significantly, carbon laydown on the catalyst may be reduced by the addition thereto of a promoter. In this invention the promoter consists of a mixture of manganese and tin. Manganese and tin in the promoter are preferably in their oxide form; each is present in amounts of about 0.05 to 5% by weight of the finished catalyst. The total weight of manganese-tin mixture present in the catalyst should be between about 0.1 to 10% by weight of the finished catalyst.

In accordance with the present invention and an integrated process for the production of benzene and para-xylene 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, para-xylene 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 para-xylene is re-established and the material may then be recycled through line 48 to crystallization unit 38 for further para-xylene 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 or 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 mol ratio between about 1 and 20 to 1.

The present invention is exemplified by the following table. Columns 4 and 5 represent runs with the catalysts of this invention, chromia and vanadia on synthetic mordenite (Zeolon), each catalyst containing manganese and tin oxides as a promoter. Columns 1, 2 and 3 are runs with catalysts made up of chromia on boria-alumina, silica-alumina, and Type Y or mordenite molecular sieve.

FEED: TOLUENE

Catalyst	Run				
	1	2	3	4	5
	Cr ₂ O ₃ , SiO ₂ -Al ₂ O ₃	Cr ₂ O ₃ , B ₂ O ₃ -Al ₂ O ₃	Cr ⁺³ , Type Y	Cr ⁺³ , MnO ₂ -SnO ₂ , Zeolon	V ⁺⁴ , MnO ₂ -SnO ₂ , Zeolon
Conditions:					
Temp., ° F.....	1,050	1,000	1,000	900	900
Pressure, p.s.i.g.....	400	800	800	500	500
LHSV.....	1	1	1	1	1
H ₂ /H ₁ C.....	2.0	2.0	1.2	2.0	2.0
Liquid recovery: Wt. percent feed.....	45	93	98	90	91
Prod. dist.:					
< Benzene.....	0.1	3.7	0.2	2.0	1.6
Benzene.....	13.9	16.1	17.1	22.8	23.4
Toluene.....	79.4	71.1	69.1	41.8	43.5
Xylene.....	6.6	9.1	13.8	27.4	27.1
> Xylene.....				1.0	4.4

¹ 5% Cr₂O₃; 2% Sn; 2% Mn.

² 5% VO; 2% Sn; 2% Mn.

From the table it is readily apparent that the yield of benzene using the catalyst of this invention is substantially improved, as is the yield of aromatics heavier than toluene.

The term "alkyl transfer" of alkyl aromatics as used herein is meant to include disproportionation and trans-alkylation. 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, 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 ring or the alkyl side chain and rearrangement of splitoff 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 cycloparaffins and like reactions.

What is claimed is:

1. A process for the alkyl transfer of alkyl aromatics; comprising, contacting an alkyl aromatic feed material with a catalyst comprising about 1 to about 20% by weight of the finished catalyst of a first metal selected from the group consisting of chromium and vanadium and about 0.05 to 5% of manganese and about 0.05 to 5% of tin each by weight of the finished catalyst deposited on a synthetic zeolite base having a silicon-to-aluminum ratio below about 5:1, while maintaining a temperature of about 700 to 1050° F., about 0 to 2000 p.s.i.g., a liquid hourly space velocity of about 0.1 to 10 and a hydrogen-to-hydrocarbon mol ratio of between 1 and 10 to 1, to cause alkyl transfer of said alkyl aromatics.

2. A process in accordance with Claim 1 wherein the first metal is vanadium.

3. A process in accordance with Claim 1 wherein the first metal is chromium.

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

5. A process in accordance with Claim 4 wherein unconverted toluene is separated from the alkyl transfer

product and the said unconverted toluene is recycled to the disproportionation step.

6. A process in accordance with Claim 4 wherein xylenes are separated from the alkyl transfer product and para-xylene is separated from said xylenes.

7. A process in accordance with Claim 6 wherein the xylenes remaining after the separation of para-xylene are subjected to isomerization and a temperature of about 500 to 900° F., a pressure of about 50 to 2000 p.s.i.g., a liquid hourly space velocity of about 0.1 to 10 and in the presence of hydrogen and a mol ratio of about 1 to 20 moles hydrogen per mole of hydrocarbon to produce additional para-xylenes.

8. 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.

9. 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 an inert atmosphere under conditions sufficient to reactivate the catalyst.

10. A process for the alkyl transfer of alkyl aromatics; comprising contacting an alkyl aromatic feed material with a catalyst consisting essentially of about 1 to 20% by weight of the finished catalyst of a metal selected from the group consisting of chromium and vanadium, and about 0.05 to 5% of manganese and 0.05 to 5% of tin each by weight of the finished catalyst deposited on a synthetic zeolite base having a silicon-to-aluminum ratio below about 5 to 1, while maintaining a temperature of about 700 to 1050° F., about 0 to 2000 p.s.i.g., a liquid hourly space velocity of about 1 to 10, and a hydrogen-to-hydrocarbon mol ratio between about 0.5 and 10 to 1, to cause alkyl transfer of said alkyl aromatics.

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