

[54] **HYDRODEALKYLATION PROCESS WITH CATALYST OF GROUP VIB METALS PROMOTED BY TIN OXIDE OR LEAD OXIDE**

3,325,504	6/1967	Grasselli .....	252/469 X
3,326,819	6/1967	Newman .....	252/469 X
2,858,348	10/1958	Bosmajian et al.....	260/668
2,780,584	2/1957	Doumani .....	260/683.3 X

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[58] **Field of Search** .....260/672; 252/455, 457, 458, 252/462, 465, 467-470, 472-474

[56] **References Cited**

**UNITED STATES PATENTS**

2,734,929	2/1956	Doumani .....	260/672
2,958,643	11/1960	Friedman.....	208/60
3,197,518	7/1965	Chapman et al.....	260/668
3,197,523	7/1965	Michalko et al.....	260/672
2,408,146	9/1946	Kearby.....	260/462 X
2,418,888	4/1947	Kearby.....	260/468 X
3,259,652	7/1966	Sachtler et al. ....	252/469 X

[57] **ABSTRACT**

A process for the hydrodealkylation of alkyl-substituted aromatic hydrocarbons, including contacting the alkyl-substituted aromatic hydrocarbons with a catalyst comprising a metal of Group VIB of the Periodic System, such as chromium, molybdenum and tungsten, in an amount from about 5 to 15 percent by weight based on the finished catalyst and a promoter comprising a metal of Group IVA of the Periodic System, such as tin and lead, in an amount between about 1 to 15 percent by weight of the final catalyst, both deposited on an inert oxide support, such as gamma aluminas, silica-alumina, magnesia-alumina, etc., at a temperature of about 1,050° to 1,200° F, a pressure of about 100 to 1,000 psig., a liquid hourly space velocity of about 0.1 to 5 and a hydrogen-to-hydrocarbon mole ratio between about 3 and 15 to 1. A second promoting agent selected from the Group consisting of alkali metals, alkaline earth metals, and rare earth metals, such as potassium, rubidium, cesium, calcium, strontium, barium, cerium, thorium, etc., may also be deposited on the carrier.

**9 Claims, No Drawings**

## HYDRODEALKYLATION PROCESS WITH CATALYST OF GROUP VIB METALS PROMOTED BY TIN OXIDE OR LEAD OXIDE

### BACKGROUND OF THE INVENTION

The present invention relates to a process for the hydrodealkylation of alkyl aromatics to the parent aromatic hydrocarbons. More specifically, the present invention relates to a process for the hydrodealkylation of alkyl aromatic hydrocarbons to the parent aromatic hydrocarbons, utilizing a unique catalyst system.

The hydrodealkylation of alkyl aromatics has been practiced for many years. The principal processes involve the conversion of toluene and like alkyl-substituted benzenes to benzene, and coal tar light oils and coal tar methyl naphthalene to benzene and naphthalene, respectively. These processes may be catalytic or non-catalytic in nature. The non-catalytic system which involves thermal dealkylation, in the presence of hydrogen, requires high temperatures and pressures. While the catalytic processes require lower temperatures and pressures, these temperatures and pressures are still quite high and therefore result in short catalyst life. Most commercial catalytic processes employ chromia-magnesia deposited on an alumina base as a catalyst. Since the development of this catalyst, there has really been no improvement in catalysts for this reaction.

It is therefore an object of the present invention to provide a new process for the hydrodealkylation of alkyl aromatics employing a novel catalyst system. In a more specific aspect, the present invention relates to the process for the hydrodealkylation of alkyl aromatics wherein catalysts which improve conversion are employed. Another and further object of the present invention is to provide a process for the hydrodealkylation of aromatics wherein catalysts of higher selectivity are utilized. A still further object of the present invention is to provide an improved process for the hydrodealkylation of alkyl aromatics wherein catalysts which reduce carbon lay-down on the catalyst are employed. A further object of the present invention is to provide an improved hydrodealkylation process for the hydrodealkylation of alkyl aromatics wherein novel catalysts are employed which permit operation at lower than conventional temperatures. Another and further object of the present invention is to provide an improved system for the hydrodealkylation of alkyl aromatics wherein catalysts are employed which permit the use of lower hydrogen partial pressures.

### SUMMARY OF THE INVENTION

Briefly, in accordance with the present invention, alkyl aromatic hydrocarbons are hydrodealkylated by contacting the alkyl aromatics with a catalyst comprising a metal of Group VIB of the Periodic System and a promoter of Group IVA of the Periodic System and these materials in combination with additional promoters selected from the group consisting of alkali metals, alkaline earth metals, and rare earth metals.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

A suitable feedstocks for use in accordance with the present invention include toluene, polymethyl benzenes, coal tar light oils, coal tar methylnaphthalene concentrates, and bicyclic concentrates from light cycle oils and heavy reformates. Feedstock preparation includes fractionation to remove front ends or bottoms to thereby remove undesired fractions such as unsaturates, indanes and resinous materials. For example, it has been found that coal tar methylnaphthalene concentrates, as received from the coke oven, contain a large amount of contaminants, such as polymers, resins and free carbon. Distillation of such raw materials to yield a 90 percent overhead leaves these materials as a bottoms. Hydrogenation and hydrotreating of the overhead fraction removes sulfur, nitrogen and oxygen contaminants, but, due to the thermal instability of the feedstocks, a heavy resinous material is produced through thermal polymerization. Distillation of the

hydrotreated product is required to remove these resins and thereby reduce carbon lay-down on the hydrodealkylation catalyst and reduce hydrogen consumption due to hydrocracking of the resins and polymers.

The processing conditions for the hydrodealkylation reaction of the present invention include a temperature between about 1,050° and 1,200°F, a pressure between about 100 and 1,000 psig., a liquid hourly space velocity between about 0.1 and 5, and a hydrogen-to-hydrocarbon mole ratio of about 3 to 15/1.

The catalysts to be employed in accordance with the present invention include metal oxides from Group VIB of the Periodic System, particularly chromium, molybdenum and tungsten. Primary promoters include Group IVA metal oxides, such as tin and lead. The additional promoters include alkali metal oxides of Group I of the Periodic System, and alkaline earth metal oxides of Group II of the Periodic System, and rare earth metals. Examples of materials of this nature which may be employed include potassium, rubidium, and cesium; magnesium, calcium and strontium, and cerium and thorium, etc. The active metal and the promoter are deposited on an inert oxide support, which preferably includes a high area alumina having a boehmite, bayerite, beta, or eta crystalline form, or other aluminas, silica-alumina, silica, silica-magnesia, silica-zirconia, alumina-magnesia, etc.

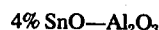
The optimum active metal content of the catalyst is about 5 to 15 percent by weight based on the final catalyst. The primary and secondary metal oxide promoters should be present in amounts of about 1 to 15 percent by weight.

The catalysts of the present invention may be prepared by well-known impregnation techniques. One may employ extrudates or pellets for impregnation or powders followed by pelletization or extrusion to yield the finished catalyst. The active metal and the promoter may be added through the use of water-soluble salts, such as their halides, nitrates, sulfates, acetates, etc. Easily hydrolyzed salts can be kept in solution without decomposition by employing appropriate inorganic acids.

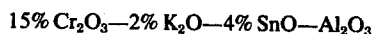
The following examples illustrate method of preparing the composite catalysts of the present invention.

#### EXAMPLE I

To 900 ml. of distilled water was added 81 g. of stannous sulfate and 30 ml. of concentrated sulfuric acid. The sulfuric acid was required to bring the insolubles from the stannous sulfate into solution. This was believed to be tin hydroxide. This solution was added to 900 ml. of a boehmite alumina as pellets and after contact for fifteen minutes, the unadsorbed liquid was decanted from the catalyst pellets. The resulting impregnated catalyst was dried at 250°F for one hour and calcined in air at 950°F for 16 hours in a muffle furnace. This yielded a catalyst of the following composition:



A solution containing 150 ml. of distilled water, 45 g. of chromic acid, and 9.5 g. of potassium nitrate was added to 150 ml. of 4% SnO—Al<sub>2</sub>O<sub>3</sub> pellets from above. Catalyst and solution was in contact for 15 minutes and the unadsorbed liquid was decanted. The resulting catalyst was dried at 250°F for 1 hour and calcined in air at 950°F in a muffle furnace for 16 hours. This yielded a catalyst of the following composition:



#### EXAMPLE II

To 600 ml. of distilled water was added 20 g. of lead nitrate. This solution was added to 600 ml. of a boehmite alumina as pellets and after contact for 15 minutes, the unadsorbed liquid was decanted from the catalyst pellets. The resulting impregnated catalyst was dried at 250°F for 1 hour and calcined in air at 950°F in a muffle furnace for 16 hours. This yielded a catalyst of the following composition:

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2% PbO—Al<sub>2</sub>O<sub>3</sub>

A solution containing 150 ml. of distilled water, 36 g. of chromic acid, and 5.5 g. of cesium nitrate was added to 150 ml. of 2% PbO—Al<sub>2</sub>O<sub>3</sub> pellets from above. Catalyst and solution was in contact for 15 minutes and the unadsorbed liquid was decanted. The resulting catalyst was dried at 250°F for one hour and calcined in air at 950°F in a muffle furnace for 16 hours. This yielded a catalyst of the following composition:

12% Cr<sub>2</sub>O<sub>3</sub>—2% Cs<sub>2</sub>O—2% PbO—Al<sub>2</sub>O<sub>3</sub>

## EXAMPLE III

To 200 ml. of distilled water was added 15 g. of cesium nitrate and 40 g. of chromic acid. This solution was added to 200 ml. of a boehmite alumina and after contact for 15 minutes, the unadsorbed liquid was decanted from the catalyst pellets. The resulting impregnated catalyst was dried at 250°F for 1 hour and calcined in air at 950°F in a muffle furnace for 16 hours. This yielded a catalyst of the following composition:

10% Cr<sub>2</sub>O<sub>3</sub>—4% Cs<sub>2</sub>O—Al<sub>2</sub>O<sub>3</sub>

## EXAMPLE IV

To 500 ml. of distilled water as added 41 g. of cerous nitrate hexahydrate and 100 g. of chromic nitrate. This solution was added to 500 ml. of a bayerite alumina and after contact for fifteen minutes, the unadsorbed liquid was decanted from the catalyst pellets. The resulting impregnated catalyst was dried at 250°F for 1 hour and calcined in air at 950°F in a muffle furnace for 16 hours. This yielded a catalyst of the following composition:

10% Cr<sub>2</sub>O<sub>3</sub>—2% Ce<sub>2</sub>O<sub>3</sub>—Al<sub>2</sub>O<sub>3</sub>

## EXAMPLE V

To 600 ml. of distilled water was added 54 g. of stannous sulfate and 20 ml. of concentrated sulfuric acid. The tin sulfate was partially insoluble and the sulfuric acid brought it into solution. This insolubility was probably due to the presence of tin hydroxide. This solution was added to 600 ml. of a boehmite alumina and after contact for 15 minutes, the unadsorbed liquid was decanted from the catalyst pellets. The resulting impregnated catalyst was dried at 250°F for 1 hour and calcined at 950°F for 16 hours to yield a catalyst of the following composition:

4% SnO—Al<sub>2</sub>O<sub>3</sub>

A solution containing 150 ml. of distilled water and 30 g. of chromic acid was added to 150 ml. of 4% SnO—Al<sub>2</sub>O<sub>3</sub> pellets (prepared as above) and allowed to remain in contact for 15 minutes before decanting the unadsorbed liquid. The impregnated catalyst was dried at 250°F for 1 hour and calcined in air at 950°F for 16 hours in a muffle furnace. This yielded a catalyst of the following composition:

10% Cr<sub>2</sub>O<sub>3</sub>—4% SnO—Al<sub>2</sub>O<sub>3</sub>

## EXAMPLE VI

A 4% SnO—Al<sub>2</sub>O<sub>3</sub> catalyst was prepared according to the procedure described in Example V. To 150 ml. of 4% SnO—Al<sub>2</sub>O<sub>3</sub> pellets was added a solution containing 150 ml. of distilled water and 1 g. of rhodium trichloride. The unadsorbed liquid was decanted and the catalyst dried and calcined according to the procedure outlined in Example I. To the rhodium oxide-tin oxide-alumina catalyst was added a solution containing 150 ml. of distilled water and 45 g. of chromic acid. The catalyst was dried and calcined (see Example I) to yield the following composition:

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15% Cr<sub>2</sub>O<sub>3</sub>—0.5% Rh—4% SnO—Al<sub>2</sub>O<sub>3</sub>

## EXAMPLE VII

By employing the techniques and procedures outlined previously, other catalytic compositions were prepared. A solution containing 600 ml. of distilled water, 54 g. of stannous sulfate and 20 ml. of concentrated sulfuric acid was added to 600 ml. of a boehmite alumina. Drying and calcination yielded to the following composition:

3% SnO—Al<sub>2</sub>O<sub>3</sub>

A solution containing 150 ml. of distilled water, 29 g. of ammonium molybdate, 10 g. of potassium nitrate, and 5 ml. of concentrated ammonium hydroxide was added to 150 ml. of 3% SnO—Al<sub>2</sub>O<sub>3</sub> pellets. Drying and calcination yielded the following composition:

12% MoO<sub>3</sub>—2% K<sub>2</sub>O—3% SnO—Al<sub>2</sub>O<sub>3</sub>

It has also been found advantageous to add trace amounts of a Group VIII metal, such as platinum, rhodium, ruthenium, palladium, nickel, etc. as a promoter. The amount of this metal should be about 0.05 to 0.5 percent by weight and the metal is preferably in its oxide form.

The following Tables illustrate the effectiveness of the present catalysts compared with a commercial chromia-magnesia on alumina hydrodealkylation catalyst.

TABLE I

Feed: Coal Tar Methyl-naphthalene

Standard Conditions: 1100°F, 500 PSIG, 0.5 LHSV, 5/1 H<sub>2</sub>/H' C

Run Catalyst Feed	1	2	3
	12Cr-1K-3Sn-Al <sub>2</sub> O <sub>3</sub>	12Cr-1K-3Sn-Al <sub>2</sub> O <sub>3</sub>	15Cr-4Sn-Al <sub>2</sub> O <sub>3</sub>
Special processing	none	topped to	topped to
product distribution		500°F	500°F
<Naphthalene*	37.2	2.50	40.4
Naphthalene	56.8	71.4	56.4
Methylnaphthalene	2.0	1.0	2.2
Dimethylnaphthalene	3.5	2.6	3.0
Wt. % Feed Me Naph.			
Conversion	87	94	86
Carbon on Catalyst			
Wt. % Feed	0.91	1.1	0.73

&lt;Naphthalene, signifies products boiling below naphthalene

TABLE II

Standard Conditions: 1100°F, 500 PSIG, 0.5 LHSV, 5/1 H<sub>2</sub>/H' C

Run Catalyst Feed	4	5	6	7	8
	Cr <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O-SnO-Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O-SnO-Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O-SnO-Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O-SnO-Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O-SnO-Al <sub>2</sub> O <sub>3</sub>
Toluene	47.7	50.6	51.6	51.6	75%
Naphthalene	33.4	32.6	48.3	48.3	25% Tetralin
Me Naphthalene	13.0	16.0	—	—	—
Di Me Naphthalene	5.8	—	—	—	—
product distribution					
<Naphthalene	42.6	47.4	52.3	44.0	80
Naphthalene	56.6	52.4	47.7	56.0	20
Me Naphthalene	0.6	0.2	—	—	—
Di Me Naphthalene	0.2	—	—	—	—
Carbon on Catalyst					
Wt. % Feed	1.5	0.96	1.60	0.20	0.05

TABLE III

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Standard Conditions: 1100°F, 600 PSIG, 0.5 LHSV, 8/1 H<sub>2</sub>/H'

Run	C		
	9 12Cr <sub>2</sub> O <sub>3</sub> - 2MgO-Al <sub>2</sub> O <sub>3</sub>	10 5Cr <sub>2</sub> O <sub>3</sub> - 10SnO-Al <sub>2</sub> O <sub>3</sub>	11 5Cr <sub>2</sub> O <sub>3</sub> - 10SnO-Al <sub>2</sub> O <sub>3</sub>
Feed	(a)	(a)	(b)
product distribution			
<Naphthalene	34.7	28.7	43.6
Naphthalene	61.7	66.2	55.9
Me Naphthalene	0.7	2.1	0.4
Di Me Naphthalene	2.9	3.0	—
Carbon on Catalyst			
Wt. % Feed	0.88	0.21	0.11
Toluene	50.4		Toluene 40.0
Naphthalene	30.4		Decalin 5.0
Me Naphthalene	13.2		Tetralin 40.0
Di Me Naphthalene	6.0		Methyldecalin 1.5
			Methyltetralin 13.5

TABLE IV

Feed: Toluene

Standard Conditions: 1150°F, 500 PSIG, 0.5 LHSV, 5/1 H<sub>2</sub>/H'

Run	C				
	12 12Cr-2Mg -Al <sub>2</sub> O <sub>3</sub>	13 15Cr-2K -4Sn-Al <sub>2</sub> O <sub>3</sub>	14 15Cr-2Cs- 2Sn- Al <sub>2</sub> O <sub>3</sub>	15 12Cr-2Cs- 2Pb- Al <sub>2</sub> O <sub>3</sub>	16 12Mo -2K-3Sn -Al <sub>2</sub> O <sub>3</sub>
liquid recovery vol. %					
Feed	84	80	81	82	82
product distribution					
<benzene	0.8	0.6	0.9	0.8	0.6
benzene	66.8	82.3	88.6	82.4	81.0
toluene	32.4	17.1	10.5	16.7	18.4
wt. % feed					
toluene					
conversion	72.8	86.3	91.5	86.3	84.9
selectivity to benzene	92	92	94	94	94
carbon on catalyst					
wt. % feed	0.26	0.014	0.02	0.04	0.08

The following Table illustrates the effect of sulfur in the feed.

TABLE V

Feed: Toluene

Standard Conditions: 1150°F, 500 PSIG, 0.5 LHSV, 5/1 H<sub>2</sub>/H'

Run	C	
	17 15Cr-2K-4Sn-Al <sub>2</sub> O <sub>3</sub>	18 0 400
Catalyst		
Sulfur, ppm	0	400
Liquid Recovery		
Vol. % Feed	80	84
Product Distribution		
<Benzene	0.6	0.5
Benzen	82.3	78.2
Toluene	17.1	21.3
Wt. % Feed		
Toluene Conversion	86.3	82.2
Selectivity to Benzene	92	96
Carbon on Catalyst		
Wt. % Feed	0.014	0.014

Further studies yielded the following results:

TABLE VI

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Feed: Coal Tar Methylnaphthalene<sup>(a)</sup>Standard Conditions: 1100°F, 500 PSIG, 0.5 LHSV, 5/1 H<sub>2</sub>/H'

Run	C	
	19 12Cr-2Mg-Al <sub>2</sub> O <sub>3</sub>	20 12Cr-1K-3Sn-Al <sub>2</sub> O <sub>3</sub>
Catalyst		
Product Distribution		
<Naphthalene	37.8	38.3
Naphthalene	59.0	55.3
Methylnaphthalene	1.4	1.6
Dimethylnaphthalene	2.9	5.1
Wt. % Feed		
Me Naphthalene		
Conversion	90	90
Carbon on Catalyst		
Wt. % Feed	1.32	0.33

(a)	Wt. %
<Naphthalene	50.4
Naphthalene	30.4
Methylnaphthalene	13.4
Dimethylnaphthalene	5.8
> DMN	—

TABLE VII

Feed: Toluene

Standard Conditions: 1150°F, 500 PSIG, 0.5 LHSV, 5/1 H<sub>2</sub>/H'

Run	C		
	21 12Cr-2Mg -Al <sub>2</sub> O <sub>3</sub>	22 10Cr-4K -Al <sub>2</sub> O <sub>3</sub>	23 10Cr-4Cs -Al <sub>2</sub> O <sub>3</sub>
Liquid Recovery			
Vol. % Feed	84	83	80
product distribution			
<Benzene	0.8	0.7	0.9
Benzen	66.8	75.6	81.8
Toluene	32.4	23.7	17.3
Wt. % Feed			
Toluene Conversion	72.8	80.2	86.2
Selectivity to Benzene	92	93	92
Carbon on Catalyst			
Wt. % Feed	0.26	0.19	0.07

TABLE VIII

Conditions: 1150°F, 500 PSIG, 0.5 LHSV, 5/1 H<sub>2</sub>/H'

Feed: Toluene

Run	C	
	24 12Cr-1Ce 3Pb-Al <sub>2</sub> O <sub>3</sub>	25 12Cr-1Sr 3Pb-Al <sub>2</sub> O <sub>3</sub>
Liquid Recovery		
Vol. % Feed	82.0	83.3
Product Distribution		
<Benzene	0.6	0.8
Benzen	74.3	71.8
Toluene	25.1	27.4
Wt. % Feed		
Toluene Conversion	79.4	77.3
Selectivity to Benzene	92	92
Carbon on Catalyst		
Wt. % Feed	0.005	0.005

TABLE IX

Run	C	
	26 351-64 10Cr-2Pb-Al	27 351-71 12Mo-4Sn-Al
Catalyst		
Feed		
Operating Conditions		
Temperature, °F	1100	1100
Pressure, PSIG	500	500
LHSV	0.5	0.5
H <sub>2</sub> /H' C, m/m	5/1	5/1
Liquid Recovery		
Vol. % Feed	81.0	80.5

Product Distribution, Vol.%		
<Naphthalene	41.0	41.4
Naphthalene	54.9	55.3
Methylnaphthalene	2.0	1.3
Dimethylnaphthalene	2.1	2.0
Wt. % Feed		
Methylnaphthalene Conversion	87	90
Carbon on Catalyst		
Wt. % Catalyst	6.95	5.90
Wt. % Feed	1.88	1.95

The following illustrate the value of adding a noble metal as a promoter.

TABLE X

Feed: Toluene					
Standard Conditions: 1150°F, 500 PSIG, 0.5 LHSV, 5/1 H <sub>2</sub> /H <sub>2</sub> C					
run catalyst	28 12Cr-2Mg -Al <sub>2</sub> O <sub>3</sub>	29 10Cr-4Sn -Al <sub>2</sub> O <sub>3</sub>	30 15Cr-4Sn -Al <sub>2</sub> O <sub>3</sub>	31 15Cr-4Sn 0.5Pt-Al <sub>2</sub> O <sub>3</sub>	32 15Cr-4Sn -Al <sub>2</sub> O <sub>3</sub>
liquid recovery vol. % feed	84	85	81.3	80	81.7
product distribution					
<benzene	0.8	0.7	1.0	0.6	0.8
benzene	66.8	74.0	79.7	75.7	81.0
toluene	32.4	25.3	19.3	23.7	18.2
wt. % feed toluene conversion	72.8	78.5	84.3	81.0	85.1
selectivity to benzene	92	96	92	90	93
carbon on catalyst wt. % feed	0.26	0.07	0.03	0.04	0.04

TABLE XI

Feed: Coal Tar Methylnaphthalene <sup>(a)</sup>					
Standard Conditions: 1100°F, 600 PSIG, 0.5 LHSV, 8/1 H <sub>2</sub> /H <sub>2</sub> C					
run catalyst	33 12Cr-2Mg -Al <sub>2</sub> O <sub>3</sub>	34 5Cr-6Sn Al <sub>2</sub> O <sub>3</sub>	35 8Cr-6Sn -Al	36 8Cr-6Sn -0.1Pt -Al <sub>2</sub> O <sub>3</sub>	37 5Cr-10Sn -Al <sub>2</sub> O <sub>3</sub>
product distribution					
<naphthalene	34.7	29.5	41.2	29.0	28.7
naphthalene	61.7	66.0	52.5	67.2	66.2
methylnaphthalene	0.7	—	0.8	0.8	2.1
dimethylnaphthalene	2.9	4.5	5.5	3.0	3.0
>DMN					
wt. % feed methylnaph. conversion	95	100	95	95	87
carbon on catalyst wt. % feed	0.88	0.23	0.18	0.41	0.21
(a)				Wt. %	
<Naphthalene				50.4	
Naphthalene				30.4	
Methylnaphthalene				13.4	
Dimethylnaphthalene				5.8	
>DMN				—	

The value of the Group IVA metals over metals of Group IVB is illustrated by the following run which should be compared with runs 29 and 30.

TABLE XII

Conditions: 1150°F, 500 PSIG, 0.5 LHSV, 5/1 H <sub>2</sub> /H <sub>2</sub> C	
Feed: Toluene	
Run Catalyst	38 10Cr-4Ti-Al <sub>2</sub> O <sub>3</sub>
Liquid Recovery	
Vol. % Feed	72.7
Product Distribution	
<Benzene	4.7
Benzene	68.9
Toluene	26.4
Wt. % Feed	
Toluene Conversion	82.1
Selectivity to Benzene	75
Carbon on Catalyst	
Wt. % Feed	0.09

25 An effort was also made to prepare a catalyst having the following composition:



30 The catalyst disintegrated completely when the titanium solution was added.

When reference is made herein to the Periodic System of the 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.

35 We claim:

1. A process for hydrodealkylating alkyl aromatic hydrocarbon materials, comprising: contacting the hydrocarbon materials with a catalyst comprising about 5 to 15 percent by weight of an active metal of Group VIB of the Periodic System and a promoting amount of about 1 to 15 percent by weight of a metal selected from the group consisting of tin oxide and lead oxide, both impregnated on a carrier consisting essentially of at least one solid, pellet-form inert oxide, under conditions sufficient to effect said hydrodealkylation reaction, including, a temperature of about 1,050° to 1,200°F, a pressure of about 100 to 1,000 psig, a liquid hourly space velocity of about 0.1 to 5, and a hydrogen to hydrocarbon mole ratio between about 3 and 15 to 1.

2. A process in accordance with claim 1 wherein about 0.05 to 0.5 percent by weight of a secondary promoting metal from Group VIII of the Periodic System is impregnated on the carrier.

3. A process in accordance with claim 1 wherein about 1 to 15 percent by weight of a secondary promoter selected from the group consisting of alkali metals, alkaline earth metals and rare earth metals is impregnated on the carrier.

4. A process in accordance with claim 3 wherein the secondary promoting metal is in its oxide form.

5. A process in accordance with claim 4 wherein about 0.05 to 0.5 percent by weight of a tertiary promoting metal from Group VIII of the Periodic System is impregnated on the carrier.

6. A process in accordance with claim 3 wherein the secondary promoting metal is an alkali metal.

7. A process in accordance with claim 3 wherein the secondary promoting metal is an alkaline earth metal.

8. A process in accordance with claim 3 wherein the secondary promoting metal is a rare earth metal.

9. A process in accordance with claim 1 wherein the inert oxide carrier is a gamma alumina.

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