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CATALYTIC DEALKYLATION OF ALKYLATED COMPOUNDS

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4 Claims. (Cl. 260—672)

1

This invention relates to catalytic dealkylation of alkylated compounds, including alkylated aromatic and paraffinic compounds.

Many compounds in the past have been subjected to dealkylation but this dealkylation becomes increasingly difficult in removing the short chain alkyl groups, such as methyl and ethyl groups, and a method for selectively removing methyl groups from a compound containing a multiplicity of methyl groups is particularly desirable.

In straight-run gasolines there is normally present a considerably larger amount of C_8, C_9 and higher aromatics than the more useful lower boiling homologues, such as benzene and toluene. Thus, in a typical East Texas straight-run naphtha, it has been found that the total aromatic portion consists roughly of 14 per cent benzene and toluene, 26 per cent xylenes and the balance high boiling aromatics (to 210° C.). Also it is found that in the operations of thermal cracking, catalytic cracking, hydroforming, etc., relatively large quantities of higher boiling aromatics are produced. These aromatics boiling above 140° C., while possessing good rich mixture sensitivity and high octane number, as do benzene, toluene and the xylenes, nevertheless, on account of their higher boiling points, can not be tolerated in substantial quantities as aviation gasoline components.

Accordingly, dealkylation may take place by passing a high boiling alkyl aromatic or a mixture, for example, an aromatic-containing petroleum cut, containing such high boiling alkyl aromatic, in vapor phase over and into contact with an activated catalyst in the presence of hydrogen. It has been found that under these conditions the alkylated aromatics can be dealkylated, with substantial conversion of, for example, xylene, pseudocumene, etc., into benzene, toluene, etc. Aside from these lower boiling aromatics, the principal product appears to be methane. The process is characterized by the following equation:

2

$$C_6H_n(R)_{6-n}+H_2\rightarrow C_6H_{n+1}\cdot R_{5-n}+R\cdot H$$

(R=alkyl)

or, in the illustrative case of xylene:

$$C_6H_4(CH_3)_2+H_2\rightarrow C_6H_5\cdot CH_3+CH_4 \quad (A)$$

It is customary in employing catalysts of the type employed in carrying out this process to maintain a hydrogen atmosphere over the catalyst when not in use. Also, in regenerating such catalysts, carbonaceous material is usually burnt off at temperatures below about 400° C., followed by reduction of the resulting oxide, e. g., nickel oxide, in a hydrogen stream.

It is an object of this invention to increase the liquid products yield in this type of reaction.

It is a further object of this invention to provide a process for dealkylation and particularly demethylation of either aromatic or aliphatic compounds.

It is a further object of this invention to provide a process for dealkylation and particularly demethylation of either aromatic or aliphatic compounds with such control as to selectively remove a single alkyl group.

These and other objects of this invention are attained by treating the compound to be dealkylated with hydrogen in the presence of a metallic catalyst of the eighth group of the periodic table at a temperature in the range 250° to 400° C.

The temperature range 250° to 400° C. embodies the operable temperature range for the dealkylation but peak efficiency is obtained in the temperature range 275° to 300° C. In commercial operation this latter temperature range is most desirable. In the case of the aromatic compounds, temperatures below 250° C. tend to cause saturation of the ring while at temperatures above 400° C. there is a greater amount of cracking than is desired.

The catalyst comprises a metal of the eighth periodic group usually supported on an inert support, such as alumina or kieselguhr. Nickel

is the most preferable metal, and this may be best used in such a manner that there is 60 to 75 per cent of nickel deposited on the catalyst support.

Operable pressures will depend upon the degree of dealkylation but will usually fall within the range of from atmospheric to about 500 pounds per square inch.

The compounds to be treated include aromatics, either monocyclic or polycyclic and aliphatics such as paraffins and olefins. Aromatic compounds include xylene, pseudocumene, mesitylene, diethylbenzene, triethylbenzene, etc. Examples of the paraffinic compounds include neohexane and 2,3,3-trimethylpentane. While the invention is directed to dealkylation generally, it is particularly directed to the dealkylation of the shorter chain alkyl groups and most particularly to the removal of a methyl group from a hydrocarbon compound.

We have found that hydrogen pretreatment of the catalyst has a markedly deleterious effect on the catalytic dealkylation of higher aromatics and aliphatics. During the initial period of reaction following hydrogen pretreatment, an incontrollable temperature rise occurs throughout the catalyst mass, amounting in some cases to 60–75° C. The total liquid recovery is appreciably lowered, extensive dealkylation to benzene occurs in the case of aromatics, the methane content of the exit gases increases greatly, sintering, and permanent impairment of the catalyst activity may occur. The overall effect of such reaction may be represented, in the exemplary case of xylene, by the equation:

$$C_6H_5(CH_3)_2+11H_2\rightarrow 8CH_4 \qquad (B)$$

It appears that as a result of prolonged hydrogen pretreatment of the catalyst, the catalyst surface is initially covered with a high hydrogen concentration which would be expected to produce extremely rapid reaction at the start of a run. This rapid reaction rate may in turn produce a catalyst temperature rise on account of excessive heat of reaction. The combination of high catalyst temperature and high surface concentration of hydrogen is probably responsible for the complete decomposition reaction.

Reaction A above shows that no gas volume change takes place therein, hydrogen consumption being balanced by methane formation. When methane-producing side reactions of the decomposition type take place (see Reaction B, supra), however, they result in a pronounced gas volume contraction. Moreover, gradually increasing contraction may take place upon long continued runs, even following hydrocarbon pretreatment according to this invention. This increase in contraction appears to be paralleled by increase in catalyst temperature.

Thus, in a continuous process, a check should be made of gas volume contraction or catalyst temperature, and the catalyst should be treated by the method of the invention when required. The method involves a pretreatment of the catalyst with an inert deactivating fluid including nitrogen-rich gases, other hydrocarbons, or the charge itself.

The following tables show the results of runs on various high boiling alkyl aromatics. The catalysts used were nickel supported or kieselguhr and containing from 60 to 70 per cent by weight of nickel. The runs were at substantially atmospheric pressure. Other details of operation are given in the tables.

Table I

Run Number	1	2	3
Charge	xylene	xylene	xylene
Moles H_2/Mole Charge	2.3	2.1	2.3
Space Velocity	0.43	0.48	0.44
Av. T., °C	308	289	272
Max. T	336	304	284
Throughput	0.86	1.15	1.03
H_2 Parts/hr.	27.4	27.6	27.5
Run Duration, min.	120	145	140
Wt. Per Cent Liq. Recovery	66.2	77.5	86.3
Products, Prod. Basis:			
Benzene, wt. per cent	5.5	7.5	4.0
Toluene, wt. per cent	24.5	28.5	23.0
Xylene, wt. per cent	70.0	64.0	73.0
Exit Gas parts/hr.	23.1	22.7	25.0
Hydrogen	8.7	11.1	64.9
Methane	90.0	86.7	33.5
Ethane+	1.3	2.2	1.6
Vol. H_2/Vol. Exit Gas	1.19	1.22	1.10

Table II

Run Number	4	5	6	7	8	9	10
Charge	diethyl-benzene	diethyl-benzene	triethyl-benzene	cumene	cumene	cumene	mesitylene
Moles H_2/Mole Charge	2.4	2.5	3.3	2.6	2.4	2.3	2.6
Space Velocity	0.53	0.51	0.46	0.44	0.47	0.49	0.44
Av. T., °C	266	283	289	277	280	295	280
Max. T	272	286	296	281	290	319	286
Throughput	1.02	1.02	0.92	0.89	0.71	0.98	0.59
Run Duration, min.	115	120	120	120	90	120	80
H_2 Parts/Hr.	27.4	27.5	27.3	27.3	27.7	27.5	27.5
Wt. Per Cent Liq. Recovery	91.6	87.4	91.2	90.7	88.1	78.6	89.4
Products, Wt. Per Cent:							
Benzene	trace	trace		trace	2.5	4.0	2.0
Toluene	1.0	3.0		5.5	7.5	9.0	8.5
Xylene	6.5	8.0	1.0	6.0	6.0	7.0	
Ethylbenzene							
Methylethylbenzene	13.5	19.0					
Mesitylene							
Diethylbenzene	79.0	70.0	7.0				89.5
Cumene							
Triethylbenzene			[1] 92.0	88.5	84.0	80.0	
Exit gas parts/hr.	27.0	26.6	26.4	26.1	25.4	23.7	26.7
Hydrogen	87.2	80.7	81.5	87.0	70.4	39.8	87.2
Methane	11.4	18.1	16.7	11.8	27.4	58.4	11.5
Ethane+	1.4	1.2	1.8	1.2	2.2	1.8	1.3
Vol. H_2/Vol. Exit Gas	1.02	1.03	1.03	1.05	1.09	1.16	1.03

[1] Contains 2% of material boiling between diethyl and triethyl benzene.

The above tables illustrate that a high degree of demethylation is secured by the process.

The following table illustrates the conditions and results obtained on a xylene charge wherein the catalyst is cobalt-thoria-kieselguhr in a weight ratio of 100–18–100:

Table III

	Run Number 11
Charge	xylene
Moles H_2/mole charge	1.9
Space velocity	0.80
Av. T., °C.	267
Max. T., °C.	269
Throughput	1.39
H_2 parts/hr.	27.5
Run duration, min.	105
Weight percent liq. recovery	95.3

Products, prod. basis:	Run Number 11
Benzene, weight percent	2.0
Toluene, weight percent	8.5
Xylene, weight percent	89.5
Exit gas parts/hr	26.1
Hydrogen	86.1
Methane	11.8
Ethane+	2.1
Vol. H_2/vol. exit gas	1.05

In the following table are shown results of three runs (12, 13, 14) of xylene dealkylation of the usual, initial highly exothermic type of reaction with hydrogen treated catalyst and for comparison two runs (15, 16) on the subsequent stage of the reaction after the catalyst temperature had subsided. These runs were carried out with an initial catalyst temperature of 305° C. and a hydrogen to xylene ratio of 4.2–4.4:1. The catalyst was nickel supported on kieselguhr.

Table IV

Run Number	12	13	14	15	16
Average Temperature, °C.	337	326	339	312	313
Maximum temperature, °C.	371	374	390	316	316
Liquid Space Velocity	0.37	0.36	0.38	0.36	0.36
Throughput, Vols./vol. cat.	0.37	0.42	0.35	1.14	1.26
Liquid Product:					
Liquid Recovery, Vol., per cent	68.4	71.4	66.9	93.9	90.9
Benzene, Vol., per cent	------	[1]26.5	------	4.5	4.1
Toluene, Vol., per cent	------	[1]39.5	------	28.5	31.9
Hydrogen Charged, parts	21.5	24.9	19.5	67.7	74.8
Exit Gas, parts	18.9	22.7	17.4	68.1	74.9
Hydrogen, per cent	------	39.8	6.5	------	87.2
Methane, per cent	------	57.9	91.2	------	10.6
Ethane, per cent	------	2.39	2.3	------	2.2
Efficiency, per cent	80	80	80	98	98

[1] Three runs (12, 13, and 14) combined for distillation analysis.

From the above runs, it is evident that while a high degree of demethylation is secured following hydrogen pretreatment, a high ultimate recycle yield could not be obtained under these conditions, because of the low liquid recovery.

Various other runs which were conducted illustrate that the higher hydrogen to hydrocarbon mole ratios give higher conversions. Thus while hydrogen-to-hydrocarbon mole ratios in the range of 1:1 and 5:1 are desirable, a ratio of about 4:1 is preferable.

The following table gives the results of a series of runs carried out at an initial temperature of 305° C. and with hydrogen-xylene ratios of

4.2–4.8:1, in which the catalyst (same as that described in Table I) was pretreated with xylene alone before the first run (liquid throughput 0.12). Cumulative throughputs (i. e. volumes of liquid xylene per volume of catalyst) are tabulated and the data under the throughput entries refer to the average yields and temperature for the run periods shown. Between successive runs, the catalyst was maintained in a hydrogen atmosphere at 305° C. This hydrogen treatment was in all cases of such duration as would normally produce a highly exothermic initial reaction.

Table V

Run Number	17	18	19	20	21	22	23
Cumulative Throughput Intervals (Vols. of xylene per vol. of Catalyst)	0.12 to 0.56	0.56 to 0.89	0.89 to 1.79	1.79 to 2.83	2.83 to 3.88	3.88 to 5.00	5.00 to 6.11
Liquid Recovery, Vol. Per cent	95.0	87.4	89.0	84.1	88.0	86.6	86.2
Per cent Methane in Exit Gas	3.4	7.0	7.2	20.1	16.2	31.6	23.6
Benzene, Vol. Per cent	trace	0.5	3.3	4.5	6.5	9.0	10.0
Toluene, Vol. Per cent	16.0	10.3	26.2	35.0	35.0	36.7	37.5
Maximum Temp., °C.	314	315	314	320	320	329	328
Hydrogen Charge/Exit Gas	0.994	0.999	0.986	1.009	1.023	1.046	1.012
Av. Cat. Temp	312	312	312	317	317	319	319

While catalyst activity is somewhat reduced by the hydrocarbon pretreatment, normal activity is restored after a liquid throughput of about 2.0, and in no case does the exothermic reaction produce a temperature rise of more than 15° C. The trend toward increased temperature may be counterbalanced by a periodic hydrocarbon treatment of the catalyst.

By a comparison of Tables IV and V, it will be seen that an increased liquid recovery is attained with the xylene pretreatment of the catalyst.

Table VI shows results obtained with the alternative expedient of following hydrogen reduction with pretreatment of the catalyst (same as in preceding table) in a nitrogen stream. In the three examples, the catalyst was pretreated at 305° C. for 18 hours in a nitrogen stream. Between each run, i. e. between 24 and 25, and 25 and 26, sufficient hydrogen was passed over the catalyst normally to produce an initial decomposition reaction. The hydrogen-xylene ratios were as in the preceding table.

Table VI

Run Number	24	25	26
Average Temperature, °C.	311	312	314
Maximum Temperature, °C.	315	314	316
Liquid Space Velocity	0.36	0.37	0.36
Throughput, Vol./Vol. Cat.	1.27	1.28	1.16
Liquid Product:			
Liquid Recovery, Vol. per cent	94.5	92.1	90.8
Benzene, Vol. per cent	3.5	3.5	5.5
Toluene, Vol. per cent	23.5	29.5	33.5
Hydrogen Charged, parts	74.8	75.1	69.5
Exit Gas, parts	74.8	75.4	70.1
Hydrogen	90.5	87.7	85.2
Methane	8.0	10.0	12.7
Ethane+	1.5	2.3	1.9
Efficiency, per cent	98	98	98

It is manifest from the two preceding tables that where the catalyst has been pretreated, for example, with hydrocarbon charge alone or with nitrogen, there is no appreciable gas volume contraction. However, subsequent prolonged treatment of the catalyst with hydrogen will again produce a contraction.

Following run 26, the catalyst was subjected to a hydrogen treatment 23 times that normally required to produce the exothermic reaction. The results are shown in the following table:

Table VII

	Run Number 27
Average temperature, °C	344
Maximum temperature, °C	385
Liquid space veocity	0.38
Throughput, vols./vol. cat	0.50
Liquid product:	
Liquid recovery, vol. per cent	62.1
Benzene, vol. per cent	23.6
Toluene, vol. per cent	34.3
Hydrogen charges, parts	28.7
Exit gas, parts	24.7
Hydrogen	25.0
Methane	72.3
Ethane+	2.7
Efficiency ——per cent	71

The hydrogen-xylene ratio was the same as in Table V. A considerable contraction in gas volume, and a marked rise in temperature are evident.

In the above Tables IV, VI and VII are given per cent efficiencies. These are calculated as the moles of liquid product divided by the moles of charge times 100. During the highly exothermic reaction shown in runs 12, 13 and 14 efficiency was relatively low. Run 27 has a very low efficiency since it is an example where the catalyst was purposely pretreated with hydrogen.

When this highly exothermic phase does not occur, the efficiency is quite high. Where the catalyst had been previously flushed with nitrogen, as in runs 24, 25 and 26, efficiency was 98 per cent. Similarly, the series of runs shown in Table V had an average efficiency of 95 per cent. In runs of relatively long duration after the exothermic reaction has run its course, high efficiency may subsequently be attained as in runs 15 and 16 where the average efficiency was 98 per cent.

What we claim is:

1. In a process for catalytically dealkylating a high boiling alkyl aromatic hydrocarbon into a lower boiling homologue while in contact with hydrogen, a metallic catalyst of the eighth group of the periodic table, and at a temperature in the range 250° to 400° C., the step which comprises treating the catalyst in the absence of hydrogen with said high boiling alkyl aromatic hydrocarbon.

2. The method of dealkylating a high boiling alkyl aromatic hydrocarbon into a lower boiling homologue which comprises contacting a mixture containing hydrogen and the said hydrocarbon with an activated nickel catalyst at a temperature of 250°–400° C., and periodically eliminating the hydrogen from the mixture while continuing contact between the catalyst and the alkyl aromatic hydrocarbon.

3. The method of converting a high boiling alkyl aromatic hydrocarbon into a lower boiling homologue which comprises passing a mixture of hydrogen and the said hydrocarbon over an activated nickel-on-kieselguhr catalyst at a temperature of 250° to 400° C., and periodically replacing the said mixture by a current of nitrogen gas.

4. The method of dealkylating a high boiling alkyl aromatic hydrocarbon into a lower boiling homologue which comprises contacting a mixture containing hydrogen and the said hydrocarbon with an activated dealkylation metal catalyst of the eighth group of the periodic system at a temperature of 250° to 400° C., periodically testing the catalyst temperature, and periodically treating the catalyst in the absence of hydrogen with a fluid which will remove hydrogen from the surface of the catalyst and thus reduce its activity whenever said catalyst temperature reaches a predetermined maximum.

CHARLES W. MONTGOMERY.
WILLIAM A. HORNE.

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Certificate of Correction

Patent No. 2,470,712. May 17, 1949.

CHARLES W. MONTGOMERY ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 4, line 21, for the words "supported or" read *supported on*; column 5, Table IV, under the heading "13", next to the last line, for "2.39" read *2.3*; column 7, line 5, Table VII, for "veocity" read *velocity*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 11th day of October, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.