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UPGRADING GASOLINE AND NAPHTHA

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This application is a continuation-in-part of our application Serial No. 198,468, filed November 30, 1950.

The present invention relates to improvements in catalytic reforming of hydrocarbon distillates boiling approximately in the range of gasoline and is particularly concerned with novel catalysts of high selectivity for use in such process and the particular method of preparation by which such catalysts may be obtained.

One of the principal objects of the invention is the provision of an improved catalyst capable of producing high yields of gasoline of desired enhanced octane quality and of good lead susceptibility, while minimizing the occurrence or extent of such other accompanying reactions, such as cracking, which tend to produce coke and low molecular weight hydrocarbon gases, at the expense of desired gasoline yields.

In previous known processes for upgrading gasoline and naphtha fractions, involving treatment at superatmospheric pressure and in the presence of added hydrogen, catalysts have been employed having the property of promoting dehydrogenation reactions, the best known being molybdenum oxides on activated alumina. While under the conditions employed in these previous processes dehydrogenation of naphthenes present in the gasoline charged to reforming does take place, other simultaneous reactions occur to substantial extent, including cracking of parts of the charge, resulting in the formation of significant quantities of low molecular weight hydrocarbon gases accompanied by deposition of coke in sufficient amounts to limit the practical on-stream operating period to about 4-8 hours, followed by regeneration of the catalyst. The reported butane-free gasoline yields from such processes are in the order of about 70-80% by volume of the charge. In other related processes conditions were employed to dehydrogenate selected narrow cuts of naphthenic materials to aromatic hydrocarbons, operating under conditions obtaining lower conversion of the charge per pass, and generally at higher pressures (up to about 50-70 atmospheres) than the previously described process. In these processes operating at lower conversion levels longer on-stream periods of up to several days or more might be possible, requiring as much as about 20-24 hours for regeneration of the coke produced. Reformatted products high in aromatic content are stated to be obtained, but the overall gasoline yields are not substantially better than those obtained in

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the previously described processes carried out at lower pressure.

In accordance with the present invention, naphthenes in gasoline and naphtha fractions, are selectively converted to aromatics under conditions disfavoring accompanying production of undesirable side products such as coke and gas. This desirable result is brought about by carrying out the reforming process in the presence of a catalyst consisting essentially of a minor proportion of molybdenum oxide well distributed over the available surface of an alumina carrier which has been previously treated to render the carrier substantially devoid of cracking or polymerizing-promoting function. Such catalysts are prepared in accordance with the invention by treating alumina with magnesium compounds which are converted to magnesia, the conditions of treatment being controlled to avoid formation of so called "beta alumina." This treatment results in the production of an alumina base or carrier having no significant cracking activity. Molybdena is then incorporated in the specially prepared carrier in known or suitable manner.

The catalyst thus prepared is employed in reforming of gasoline and naphtha distillates in the presence of added hydrogen, at pressure of 200-1000 p. s. i., temperatures between about 850-1000° F., the hydrocarbon distillate being charged at a liquid space rate of preferably not less than 1 volume per hour per volume of catalyst. Preferred operating conditions include temperatures not in excess of about 950-975° F. and liquid space rates of at least 2.

The catalysts employed in the reforming processes of the invention are highly selective in promoting dehydrogenation of naphthenes but have little or no activity in promoting cracking of hydrocarbons. The selectivity of various catalysts can be tested by their separate effects on conversion of heptane and of methylcyclohexane under standardized conditions. The catalysts of the invention as contrasted with typical commercial dehydrogenation catalysts of the molybdena-alumina type or catalysts of the chrome-alumina type, are characterized by high rates of conversion of methylcyclohexane to aromatics without accompanying production of large amounts of by-products such as coke and gas and by their relatively low activity in the conversion of normal heptane. Since dehydrocyclization of normal heptane involved is associated with a course of reaction including a cracking function, the characteristic behavior of the catalysts of the

invention is indicative of high selectivity for promoting dehydrogenation of hydroaromatic naphthene compounds without material tendency to promote accompanying side reactions such as carbon-carbon scission and polymerization.

Activated alumina of commerce as well as heat-treated bauxite already possesses significant cracking activity. By the incorporation of molybdena in known manner in such aluminaeous carriers the cracking activity of the composite may be further increased. In the catalysts of the present invention, however, the cracking promoting function of the carrier is materially attenuated or destroyed, to provide the desired selectivity for dehydrogenation.

The reforming process of the invention is applicable to the treatment of various naphtha charge stocks containing naphthenes of the hydroaromatic type, including catalytically cracked distillates as well as straight run gasoline and naphthas and distillates from thermal cracking. An important application of the invention is in the treatment of gasoline and naphtha fractions derived from hydrogenative processes such as hydrogenative cracking and destructive hydrogenation, which fractions are generally characterized by a high naphthene content and low octane rating.

It is important that the magnesia be incorporated in the alumina prior to the incorporation of the molybdena. Catalysts prepared by treatment of molybdena-alumina with magnesia do not have the same high selectivity of the catalysts of the invention and characteristically obtain lower gasoline yields and produce significantly larger quantities of coke than the catalysts of the invention. This observed difference in behavior of the two catalysts can not be entirely satisfactorily explained. The reason that known hydroforming catalysts comprising molybdena on activated alumina tend to produce coke and low molecular weight gases appears to be related to cracking activity. The cracking-promoting function is believed to be centered on acid sites existing in these catalysts or is related to their ability to accommodate or transfer protons. By base-exchanging or treating such active sites with appropriate cations the "acidity" or protonic activity and accordingly the cracking function can be inhibited.

The catalysts of the invention are prepared by treating calcined or activated alumina in lump or tablet form with an aqueous solution of a soluble magnesium compound and drying the product. The effect of this treatment is already noticeable when as little as 0.05% magnesia is incorporated in the alumina; quantities of magnesia above about 2-3% do not appear to have any added useful effect and may be undesirable. Preferably about 0.1 to 2.0% magnesia by weight is employed.

The dried magnesia-alumina is dipped in a solution of a molybdenum salt, such as ammonium molybdate, and the salt decomposed to the oxide. The molybdena may be present in proportions of about 7.0 to 15.0% by weight of the final catalyst. It is important that the alumina, before or after deposition of the molybdenum compound, be not heated to high temperatures or otherwise treated to cause transformation thereof to beta forms of alumina.

Prior to being placed on-stream the catalyst is treated in a stream of reducing gas such as hydrogen to transform the molybdenum oxides to lower valence state.

EXAMPLE I

Commercial activated-alumina tablets (Harsaw) were treated with 20% magnesium chloride ($MgCl_2$) solution, using about 5 liters solution per kilogram of alumina, then washed free of chlorides and dried. The dried product was treated for thirty minutes with a solution of ammonium molybdate (calculated to deposit 10% MoO_3 on the alumina) containing about 270 grams MoO_3 per liter of water, in the proportions of about 400 milliliters solution per kilogram of alumina. The treated product was drained, dried, and heat treated at 1050° F. for two hours. Before being placed on stream, hydrogen was passed over the catalyst to reduce the molybdena to lower valence forms. The final catalyst contained 0.28% MgO .

The catalyst thus prepared was employed in reforming East Texas naphtha with the following results:

Table 1

Charge: East Texas naphtha.
B. R. 240-352° F., API° 53.3.
Catalyst: MoO_3 on magnesia-treated alumina.

Operating conditions:			
Pressure, p. s. i. g.	600	600	750
Temp., ° F.	950	950	950
LSV (vol./hr./vol.)	2	4	2
H ₂ oil ratio	3	5	3
Yields:			
Gasol. (C_5+), vol. percent	86.5	91.3	88.8
C ₄ , vol. percent	8.1	4.4	7.2
Dry Gas, wt. percent	4.1	3.2	3.8
Coke, wt. percent	0.4	.007	0.6
Octanes:			
CFR-R clear	85.3	75.0	79.5
+3 cc. TEL	95.4	88.4	93.2

EXAMPLE II

An Al_2O_3 - MgO - MoO_3 catalyst was prepared following the procedure of the preceding example using about the same proportions of components, and likewise tested in reforming the previously reported naphtha in a series of runs with the following results:

Table 2

Operating conditions:			
Pressure, p. s. i. g.	600	600	
Temp., ° F.	950	950	
LSV (vol./hr./vol.)	2	4	
H ₂ oil ratio	3	3	
Yields:			
Gasol. (C_5+), vol. percent	82.8	84.8	
C ₄ , vol. percent	11.2	10.1	
Dry Gas, wt. percent	4.9	4.0	
Coke, wt. percent	0.4	0.2	
Octanes:			
CFR-R clear	87.8	88.6	
+3 cc. TEL	97.1	95.6	

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim as our invention:

1. The method of upgrading the quality of a naphtha fraction containing naphthenic hydrocarbons boiling in the range of gasoline, which comprises contacting such a fraction in the presence of added hydrogen with a catalyst consisting of molybdenum oxide incorporated in an inert non-acidic carrier consisting essentially of gamma alumina containing up to about 3% amorphous magnesia incorporated therein and being substantially free of crystalline magnesium aluminate, said catalyst having been prepared by incorporation of the molybdenum oxide into the alumina carrier which has been previously impregnated with magnesia; said contacting being

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performed under conditions suitable for dehydrogenation of naphthenes in said fraction, including super atmospheric pressure and temperatures in the range of 850-1000° F.; and recovering a gasoline fraction of desired boiling range from the reformat thus distributed.

2. The method of selectively dehydrogenating naphthenic hydrocarbons in a hydrocarbon fraction boiling approximately in the range of gasoline with concomitant formation of minimized quantities of cracked products including coke and low molecular weight hydrocarbon gases, which comprises contacting said hydrocarbon fraction with a catalyst consisting of about 7-15% by weight of molybdenum oxides incorporated in an inert non-acidic carrier consisting essentially of gamma alumina containing .05-3% amorphous magnesia incorporated therein said carrier being substantially free of crystalline magnesium aluminate, said catalyst having been prepared by incorporation of the molybdenum oxide into the alumina carrier which has been previously impregnated with magnesia; said contacting being effected under reaction conditions including pressure of 200 to 1000 pounds per square inch, temperatures of about 850-1000° F., and liquid space velocity not less than 1 volume hydrocarbon fraction per hour per volume of catalyst.

3. The method of obtaining high yields of gasoline of improved octane rating which comprises charging a naphtha cut having a high naphthene content to catalytic dehydrogenation in the presence of a catalyst consisting of 7-15% by weight molybdenum oxides distributed on a carrier composed of gamma alumina containing 0.1-2% amorphous magnesia distributed therein, said catalyst having been prepared by incorporation of the molybdenum oxide into the alumina carrier which has been previously impregnated with

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magnesia, and effecting selective dehydrogenating of naphthenes in said cut in contact with said catalyst at a temperature in the range of 850-950° F., under a pressure of about 200-1000 pounds per square inch, hydrogen in excess being added to said naphtha charge, and said naphtha being charged to said dehydrogenation at a liquid space rate in excess of 1 volume per hour per volume of catalyst.

4. The method of selectively dehydrogenating naphthenic hydrocarbons contained in a gasoline fraction without production of excessive quantities of cracked products including coke and low molecular weight hydrocarbons, which comprises contacting such a gasoline fraction with a catalyst consisting of molybdenum oxide incorporated in an inert non-acidic carrier consisting essentially of gamma alumina containing up to about 3% amorphous magnesia incorporated therein and being substantially free of crystalline magnesium aluminate, said catalyst having been prepared by incorporation of the molybdenum oxide into the alumina carrier which has been previously impregnated with magnesia; said contacting being performed under dehydrogenation conditions including temperature in the range of 850-950° F., pressure of about 200-1000 p. s. i., and a liquid space velocity of at least 2 volumes of hydrocarbon charge per hour per volume of catalyst.

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