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HYDROGENATION OF AROMATICS WITH METAL PHOSPHATE-CONTAINING CATALYSTS

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ABSTRACT OF THE DISCLOSURE

Aromatics hydrogenation process using a catalyst comprising alumina, silica, a component selected from nickel and compounds thereof and cobalt and compounds thereof, a component selected from molybdenum and compounds thereof and tungsten and compounds thereof, and a component selected from titanium phosphate and zirconium phosphate.

RELATED APPLICATION

This application is a continuation-in-part of Joseph Jaffe application Ser. No. 671,994, filed Oct. 2, 1967.

INTRODUCTION

This application relates to hydrogenation of aromatic hydrocarbons.

PRIOR ART

It is known that many hydrocarbon stocks such as jet fuels, diesel fuels, gas turbine fuels, kerosene, furnace oils, lubricating oils, etc., can be upgraded by partial or complete hydrogenation of the aromatic constituents thereof.

Aromatics hydrogenation results in improved burning characteristics for many fuels. For example, in the case of jet fuels, desirable increases in smoke points can be obtained by hydrogenation of the aromatics contained in the fuels to the corresponding naphthenes, which have higher heats of combustion.

Commercial hydrofining processes directed to the removal of contaminants such as sulfur and nitrogen from hydrocarbon feedstocks inherently accomplish hydrogenation of olefin constituents of the feedstocks; however, these processes accomplish little or no hydrogenation of aromatics constituents in the feedstocks.

Aromatics hydrogenation processes are well known. Prior art hydrogenation catalysts generally comprise platinum on alumina, occasionaly with a minor proportion of added halogen. Various other Group VIII metals, such as nickel, cobalt and iron, as well as other metals of the platinum group, deposited on alumina or other suitable carriers also have been employed. The prior art processes have been carried out at temperatures within the range 300° to 900° F., pressures within the range 1000 to 5000 p.s.i.g., and liquid hourly space velocities in the range 0.1 to 20, in the presence of 2500 to 25,000 standard cubic feet of hydrogen per barrel of charged material.

Conventional aromatics hydrogenation processes are disclosed in the following representative patents: 2,967,204; 3,012,961; 3,077,733; 3,147,210; 3,172,833; 3,186,935.

Conventional aromatics hydrogenation catalysts, particularly catalysts containing Group VIII noble metals, are sulfur-sensitive, and the presence of organic sulfur compounds in the fed exerts a deleterious effect on the hydrogenation activity of these catalysts. The sulfur sensitivity of the Group VIII noble metal hydrogenation catalysts is particularly discussed in the aforesaid Pats. 3,147,210 and 3,186,935.

In view of the importance of aromatics hydrogenation for improving the burning characteristics of many aromatics-containing hydrocarbon feedstocks, there is a continuing search for improved processes for accomplishing the desired hydrogenation, particularly processes using aromatics hydrogenation catalysts having higher aromatics hydrogenation activities and/or lower fouling rates, that is, higher stabilities.

OBJECTS

In view of the foregoing, it is an object of the present invention to provide an improved aromatics hydrogenation process employing a catalyst of high activity and stability which permits the process to be operated at reasonable temperatures for long periods of time. It is a further object of the present invention to provide an aromatics hydrogenation process using a catalyst which contains less costly constituents than the conventional Group VIII noble metal hydrogenation catalysts, and which is more sulfur-tolerant than those conventional catalysts.

STATEMENT OF INVENTION

In accordance with the present invention, there is provided an aromatics hydrogenation process which comprises contacting an aromatics-containing hydrocarbon feedstock under aromatics hydrogenation conditions with hydrogen and a catalyst comprising alumina, silica, a component selected from nickel and compounds thereof and cobalt and compounds thereof, a component selected from molybdenum and compounds thereof and tungsten and compounds thereof, and a component selected from titanium phosphate and zirconium phosphate. In a preferred embodiment of the process of the present invention, the catalyst used therein contains 0.5 to 10 weight percent silica, preferably 0.5 to 5 weight percent silica, based on the total catalyst.

The aromatics hydrogenation conditions used in the process of the present invention are conventional conditions as discussed below.

FEEDSTOCKS

Hydrocarbon feedstocks which may be used to advantage in the process of the present invention include a wide range of aromatics-containing hydrocarbon feedstocks, for example light and heavy straight run gas oils, light and heavy cracked cycle oils, and various aromatic extracts.

The hydrocarbon feedstocks will contain 5 to 95%, preferably 10 to 60%, aromatics.

Cracked stocks may be obtained from thermal or catalytic cracking of various stocks, including those obtained from petroleum, gilsonite, shale and coal tar.

The organic nitrogen and organic sulfur contents of the hydrocarbon feedstocks each may range from a few parts per million to several weight percent. If desired, the feedstocks may be treated in a conventional hydrofining step to reduce the sulfur and nitrogen contents thereof, prior to being hydrogenated in accordance with the process of the present invention.

HYDROGENATION CONDITIONS

The process of the present invention may be carried out at conventional hydrogenation conditions, for example at a temperature in the range 300° to 900° F., a pressure in the range 1000 to 5000 p.s.i.g., and a liquid hourly space velocity in the range 0.1 to 20, and in the presence of 2500 to 25,000 standard cubic feet of hydrogen per barrel of charged material.

The process of the present invention may be carried out at any desired combination of conditions within the

foregoing ranges which will produce a desired degree of aromatics hydrogenation. Desirably, a combination of conditions is selected which will result in hydrogenation of more than 50 volume percent and preferably more than 90 volume percent of the aromatics present in the feedstock.

CATALYST CONSTITUENTS AND AMOUNTS THEREOF

The catalyst used in the process of the present invention will contain the following constituents in the indicated amounts:

	Wt. percent, calculated as metal
Ni or Co, generally as NiO or CoO	1–10.
Mo or W, generally as MoO_3 or WO_3	5–25.
TiO_2 or ZrO_2	5–20.
P_2O_5	3–15.
SiO_2	0.5–10, preferably 0.5–5.
Al_2O_3	At least 20.

When the catalyst used in the process of the present invention contains titanium and no zirconium, the titanium:phosphate atomic ratio will be greater than 1:1. When the catalyst used in the process of the present invention contains zirconium and no titanium, the zirconium:phosphate ratio will be greater than 1:2.

CATALYST PREPARATION

The catalyst used in the process of the present invention conveniently may be prepared by the methods set forth in copending Joseph Jaffe patent application Ser. No. 671,994. When those methods are followed, the necessary form for the catalyst used in the process of the present invention will be obtained, that is, one in which the titanium or zirconium is combined with the phosphorus as discrete particles of titanium phosphate or zirconium phosphate, dispersed through a carrier, or matrix, of the other catalyst components.

EXAMPLES

The following examples will serve to further illustrate the practice of the present invention and its advantages.

EXAMPLE 1

A catalyst containing nickel, molybdenum, titanium, phosphorus, alumina and silica (catalyst A, a catalyst for use in the process of the present invention) was prepared by the following general procedure:

(a) An aqueous solution comprising aluminum chloride, titanium tetrachloride, and acetic acid was prepared;

(b) Titanium phosphate particles were caused to precipitate from said solution by combining said solution with a second aqueous solution containing phosphoric acid, resulting in a slurry containing said titanium phosphate particles;

(c) An aqueous nickel chloride solution was added to said slurry to form a nickel-containing mixture;

(d) An aqueous solution of sodium silicate was added to said nickel-containing mixture to form a silica-containing mixture;

(e) Aqueous solutions containing ammonia and ammonium molybdate were added to said silica-containing mixture, causing coprecipitation at a pH of 6 to 6.5 of soluble metals not previously precipitated;

(f) The resulting slurry was filtered to produce a filter cake, which was washed free of soluble ions, dried and calcined, to produce the final catalyst.

EXAMPLE 2

A catalyst containing nickel, molybdenum, titanium, phosphorus and alumina, but no silica (catalyst B, a comparison catalyst) was prepared by suitable modification of the general procedure of Example 1.

EXAMPLE 3

A catalyst containing nickel, molybdenum and alumina, with no titanium, phosphorus or silica (catalyst C, a comparison catalyst) was prepared by suitable modification of the general procedure of Example 1.

EXAMPLE 4

A catalyst containing nickel, molybdenum, alumina and silica, but no phosphorus or titanium (catalyst D, a comparison catalyst) was prepared by suitable modification of the procedure of Example 1.

COMPOSITION OF CATALYSTS A, B, C AND D

		Catalyst constituents, weight percent					
Ex.	Catalyst	Ni(NiO)	Mo(MoO_3)	ToO_2	P_2O_5	SiO_2	Al_2O_3
1	A	8 (10.2)	20 (30)	10	5	4.5	40
2	B	8 (10.2)	20 (30)	10	5	----------	44.5
3	C	6 (7.6)	18 (27)	----------			65.4
4	D	8 (10.2)	24 (36)	----------		15.0	38.8

EXAMPLE 5

Catalyst A was used to hydrogenate a portion of a California light cycle oil of the following description:

Boiling range, ° F	400–600
Gravity, ° API	22.3
Organic sulfur content, wt. percent	[1] 1.27
Organic nitrogen content, p.p.m	2000
Aniline point	[2] 61.2

[1] Conventional noble metal hydrogenation catalysts inoperable on feeds with such high sulfur content.
[2] 60 volume percent aromatics, by analysis.

The hydrogenation was accomplished in a reactor under the following conditions:

Total pressure, p.s.i.g	2000
Total hydrogen supply rate, s.c.f./bbl. of hydrocarbon feed	5000
Liquid hourly space velocity, v./v. hour	1.0
Temperature, ° F	700

The product aniline point was determined to be 134 by mass spectrometer analysis, indicating that the aromatics content of the product was 17.5 volume percent.

EXAMPLE 6

Catalyst B was used to hydrogenate another portion of the same cycle oil used in Example 5, at the same conditions used in Example 5, except that because catalyst B was not as active as catalyst A, the temperature was raised in an effort to achieve a product aniline point near that of the aniline point of the product in Example 5. The temperature necessary to achieve a product aniline point of 131 was 725° F.

EXAMPLE 7

Catalyst C was used to hydrogenate another portion of the same cycle oil used in Example 5, at the same conditions used in Example 5, except that because catalyst C was not as active as catalyst A, the temperature was raised in an effort to achieve a product aniline point near that of the aniline point of the product in Example 5. The

temperature necessary to achieve a product aniline point of 131 was 730° F.

SUMMARY OF EXAMPLES 5-7

Ex.	Catalyst	Temperature, ° F.	Product aniline Point	Product aromatics content, vol. percent
5	A	700	134	17.5
6	B	725	131	20
7	C	730	131	20

EXAMPLE 8

Catalyst A again was used to hydrogenate another portion of the same cycle oil used in Example 5, at the same conditions used in Example 5, except that the temperature used was 720° F. At the beginning of an on-stream period of 80 hours, the product aniline point was determined to be 142, indicating a product aromatics content of 10.5 volume percent. At the end of said on-stream period of 80 hours, the product aniline point was determined to be 142, indicating no deactivation of the catalyst.

EXAMPLE 9

Catalyst D was used to hydrogenate another portion of the same cycle oil used in Example 5 at the same conditions used in Example 5, except that the temperature used was 720° F. At the beginning of an on-stream period of 60 hours, the product aniline point was determined to be 140, indicating a product aromatics content of 12.5 volume percent. At the end of said on-stream period of 60 hours, the product aniline point was determined to be 137, indicating a deactivation of the catalyst, and indicating that it would be necessary to raise the operating temperature to maintain a product aniline point of 140.

EXAMPLE 10

Catalyst A again was used to hydrogenate another portion of the same cycle oil used in Example 5 at the same conditions used in Example 5, except that the temperature used was 750° F. and the space velocity was 1.5. The product aniline point was determined to be 138, indicating that the aromatics content of the product was 14 volume percent.

EXAMPLE 11

Catalyst D again was used to hydrogenate another portion of the same cycle oil used in Example 5 at the same conditions used in Example 5 except that the temperature used was 750° F. and the space velocity used was 1.5. The product aniline point was determined to be 130, indicating that the aromatics content of the product was 21 volume percent.

From Examples 5 and 6 it may be seen that catalyst A is more active for aromatics hydrogenation that comparison catalyst B, a catalyst that corresponds to catalyst A except that contains no silica.

From Examples 5 and 7 it may be seen that catalyst A is more active for aromatics hydrogenation than comparison catalyst C, which contains only nickel, molybdenum and alumina.

From Examples 8 and 9 it may be seen that catalyst A is not only more active for aromatics hydrogenation than comparison catalyst D, a catalyst that contains nickel, molybdenum, alumina and silica, but no titania or phosphorus, but that catalyst A also is more stable than catalyst D.

CONCLUSIONS

From the foregoing it may be seen that the process of the present invention is effective for accomplishing a given amount of aromatics hydrogenation at a lower temperature than is possible with certain processes using different catalysts. It also may be seen that the process of the present invention is effective for accomplishing a greater amount of hydrogenation at a given temperature, for longer periods of time, than is possible with certain processes useing different catalysts. It further may be seen that the catalyst used in the process of the present invention, compared with conventional prior art aromatics hydrogenation catalysts, does not require the use of costly Group VIII noble metals, and is sulfur- and nitrogen-tolerant.

What is claimed is:

1. An aromatic hydrogenation process which comprises contacting an aromatics-containing hydrocarbon feedstock under aromatics hydrogenation conditions with hydrogen and a catalyst comprising alumina, silica, a component selected from nickel and compounds thereof and cobalt and compounds thereof, a component selected from molybdenum and compounds thereof and tungsten and compounds thereof, and a component selected from titanium phosphate and zirconium phosphate.

2. A process as in claim 1, wherein said catalyst contains 0.5 to 10 weight percent silica, based on the total catalyst.

3. A process as in claim 2, wherein said catalyst contains 0.5 to 5 weight percent silica, based on the total catalyst.

SUMMARY OF EXAMPLES 8-11

Ex.	Catalyst	LHSV	Temp., ° F.	Product aniline point, initial	Product aromatics content, initial	Product aniline point 60 hrs.	Product aromatics content, 60 hrs.	Product aniline point, 80 hrs.	Product aromatics content, 80 hrs.
8	A	1.0	720	142	10.5	142	10.5	142	10.5
9	D	1.0	720	140	12.5	137	15		
10	A	1.5	750	138	14				
11	D	1.5	750	130	21				

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