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(54) Titre : SYSTEME DE CATALYSEUR POUR LA COMBINAISON DE L'HYDROTRAITEMENT ET DE  
L'HYDROCRAQUAGE ET PROCEDE POUR ENRICHIR DES CHARGES D'ALIMENTATION D'HYDROCARBURES  
 (54) Title: A CATALYST SYSTEM FOR COMBINING HYDROTREATING AND HYDROCRACKING AND A PROCESS  
FOR UPGRADING HYDROCARBONACEOUS FEEDSTOCKS

(57) **Abrégé/Abstract:**

A physically intermixed catalyst system comprising two distinctly different catalytic particles, the first of which is a hydrodenitrification and/or hydrodesulfurization catalyst and the second of which is a relatively active hydrocracking catalyst, wherein the catalyst particles of both catalytic components are substantially the same size, that is the effective diameter of each catalyst component is substantially the same. The catalyst system of the present invention can be layered with unmixed catalysts. The novel systems of the present invention have been found to provide surprisingly good selectivity for liquid products and stability against catalyst fouling when used in combined hydrotreating and hydrocracking applications, and can therefore be used to provide a stable catalyst system which offers even heat distribution and reactor control in such applications.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/US93/03317</p> <p>(22) International Filing Date: 9 April 1993 (09.04.93)</p> <p>(30) Priority data: 07/869,666                      16 April 1992 (16.04.92)                      US</p> <p>(71) Applicant: CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p> <p>(72) Inventors: HABIB, Mohammad, M. ; 421 Canyon Court, Benicia, CA 94510 (US). WINSLOW, Philip, L. ; 154 Marigold Drive, Hercules, CA 94547 (US). MOORE, Richard, O., Jr. ; 6 Mount Palomar Court, San Rafael, CA 94903 (US).</p>	<p>(74) Agents: AMBROSIUS, James, W. et al.; Chevron Corporation, Post Office Box 7141, San Francisco, CA 94120-7141 (US).</p> <p>(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b> <i>With international search report.</i></p>	
<p>(54) Title: A CATALYST SYSTEM FOR COMBINING HYDROTREATING AND HYDROCRACKING AND A PROCESS FOR UPGRADING HYDROCARBONACEOUS FEEDSTOCKS</p>		
<p>(57) Abstract</p> <p>A physically intermixed catalyst system comprising two distinctly different catalytic particles, the first of which is a hydrodenitration and/or hydrodesulfurization catalyst and the second of which is a relatively active hydrocracking catalyst, wherein the catalyst particles of both catalytic components are substantially the same size, that is the effective diameter of each catalyst component is substantially the same. The catalyst system of the present invention can be layered with unmixed catalysts. The novel systems of the present invention have been found to provide surprisingly good selectivity for liquid products and stability against catalyst fouling when used in combined hydrotreating and hydrocracking applications, and can therefore be used to provide a stable catalyst system which offers even heat distribution and reactor control in such applications.</p>		

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01           A CATALYST SYSTEM FOR COMBINED HYDROTREATING  
02                   AND HYDROCRACKING AND A PROCESS  
03           FOR UPGRADING HYDROCARBONACEOUS FEEDSTOCKS  
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11                           BACKGROUND OF THE INVENTION

12                                   Field of the Invention  
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14

15   The present invention relates to a catalyst system and a  
16   process for combined hydrotreating and hydrocracking  
17   operations in a single reactor bed by contacting a  
18   hydrocarbonaceous feedstock with hydrogen under  
19   hydrocracking conditions in the presence of an appropriate  
20   dual function catalyst system. In particular, the catalyst  
21   system and process of this invention relate to a combined  
22   denitrification and/or desulfurization hydrotreating process  
23   and a hydrocracking process wherein the catalyst system  
24   exhibits surprising stability and high selectivity for  
25   liquid products boiling in the transportation fuels range.  
26   The catalyst system can be tailored to provide previously  
27   unavailable flexibility with regard to the selection of the  
28   hydrocracking catalyst.

29

30   The dual function catalyst system of the present invention  
31   comprises two randomly intermixed particulate catalysts  
32   having distinctly different catalytic functions. The first  
33   catalyst is a conventional hydrodenitrification and/or  
34   hydrodesulfurization catalyst having substantially no

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01 cracking activity. The second catalyst is a conventional  
02 zeolitic hydrocracking catalyst. Both catalysts are  
03 selected so that they are substantially the same size, that  
04 is, the effective diameter for each catalyst particle is  
05 substantially the same.

06

07 The novel catalyst systems of the present invention have  
08 been found to provide surprisingly good selectivity for  
09 liquid products and stability against catalyst fouling when  
10 used in combined hydrotreating and hydrocracking  
11 applications, and can therefore be used to provide a stable  
12 catalyst system which offers even heat distribution and  
13 reactor control in such applications.

14

15

#### Objects of the Invention

16

17 Of the many hydroconversion processes known to the petroleum  
18 refining industry, catalytic hydrotreating and catalytic  
19 hydrocracking are perhaps the two most widely applied and  
20 important. In conventional refining practice, hydrotreating  
21 is carried out using a catalyst(s) having as the principle  
22 function the removal of nitrogen and/or sulfur, that is  
23 catalytic hydrodenitritification and hydrodesulfurization.  
24 The product of hydrotreating is then fed to a hydrocracking  
25 process unit which uses catalysts having as the principle  
26 function hydroconversion to produce liquid products boiling  
27 in the transportation fuels range.

28

29 Hydrotreating the feedstock to a hydrocracking process unit  
30 is particularly important as nitrogen and sulfur are known  
31 to contaminate conventional hydrocracking process catalysts.  
32 Thus, hydrotreating is used to lower the nitrogen and sulfur  
33 content of the hydrocarbonaceous feedstock stream to an  
34 acceptable level before subjecting the hydrocarbons to the

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01 complete hydrocracking process. In general, it is desirable  
02 to lower the nitrogen content of the hydrocarbon feedstock  
03 stream to less than 50 parts per million by weight (ppm),  
04 preferably less than about 10 ppm and in many cases for  
05 increased catalyst life to a level of less than 2 ppm or  
06 even as low as about 0.1 ppm. Similarly, it is generally  
07 desirable to lower the sulfur content of the hydrocarbon  
08 feedstock stream to less than about 0.5% by weight percent,  
09 preferably less than about 0.1%, and in many cases as low as  
10 about 1 ppm.

11  
12 However, hydrotreating catalysts have various disadvantages.  
13 Perhaps the most noted disadvantage is the tendency to foul  
14 with coke or other contaminants at an excessive rate. This  
15 results in shorter catalyst life than is desirable. As the  
16 catalyst fouls or deactivates, the denitrification process  
17 temperature must be increased to maintain activity. When  
18 the maximum temperature allowed by process and equipment  
19 limitations is reached, the catalyst must be replaced or  
20 regenerated.

21  
22 A variety of measures have been suggested to overcome the  
23 problems of catalyst deactivation in hydrotreating systems.  
24 For example, U.S. Patent 4,990,243 issued February 5, 1991  
25 to Winslow describes a layered catalyst system for  
26 hydrodenitrification. The idea behind layered systems is to  
27 provide a catalyst system which permits the operator to  
28 control the process conditions such as temperature to allow  
29 more uniform operations while removing contaminants such as  
30 nitrogen. In particular, the layered systems utilize  
31 discrete catalyst layers with differing catalysts having  
32 differing activity for denitrification and cracking. The  
33 first layer is a more active denitrification catalyst which  
34 does not induce cracking reactions. The second layer is

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01 more acidic and has higher cracking activity which results  
02 in effective conversion of the refractory nitrogen compounds  
03 not converted in the first layer.

04

05 U.S. Patent 4,534,852 issued on August 13, 1985 to  
06 Washecheck et al. describes a single stage hydrotreating  
07 process for converting pitch to conversion process  
08 feedstock. According to this process the pitch containing  
09 feedstock is contacted with hydrogen and passed downwardly  
10 through a hydrotreating zone over a stacked-bed catalyst.  
11 The upper bed contains a high activity hydrotreating  
12 catalyst, and a separate lower bed contains a high activity  
13 desulfurization catalyst. The reaction product is a  
14 suitable hydrocracking feedstock.

15

16 U.S. Patent 3,923,638 issued on December 2, 1975 to  
17 Bertolacini et al. describes a two-catalyst hydrocracking  
18 process. In this process a nitrogen containing feedstock is  
19 denitrified in a pretreatment zone using a  
20 hydrodenitrication catalyst. The denitrified effluent is  
21 passed to a hydrocracking zone. The process can be carried  
22 out in a single stage.

23

24 As noted previously the product from hydrotreating can be  
25 fed to a hydrocracking process unit. Modern hydrocracking  
26 catalysts are generally based on zeolitic materials which  
27 may have been adapted by techniques like ammonia ion  
28 exchange and various forms of calcination in order to  
29 improve the performance of the hydrocracking catalysts based  
30 on such zeolites. In nearly all cases, hydrocracking  
31 catalysts are formulated to provide varying degrees of  
32 cracking activity depending upon the desired product slate.  
33 Thus, hydrocracking catalysts which have high activity, and  
34

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01 therefore promote the exothermic cracking reactions, may not  
02 be suitable for all applications.

03

04 Accordingly, the general approach of catalyst manufacturers  
05 has been to offer a family of catalysts tailored in activity  
06 for various applications. In other words, operating  
07 flexibility is achieved by selecting from a variety of  
08 available catalysts the one catalyst which is most suitable  
09 for the specific application at hand. However, this  
10 solution has created another difficulty. Refiners have  
11 found that on occasion the product slate changes which they  
12 wish to make are not possible if the choice of available  
13 hydrocracking catalysts in inventory does not include the  
14 particular catalyst with the activity required to produce  
15 the new product slate.

16

17 Thus, it would be desirable to provide a stable  
18 hydrotreating catalyst system with high denitration  
19 and/or desulfurization activity which could be used to  
20 produce a low nitrogen low sulfur feedstock to a  
21 hydrocracking process. It would also be desirable to  
22 provide a flexible hydrocracking catalyst system which had  
23 high selectivity for liquid products.

24

25 It would be even more desirable to provide a stable catalyst  
26 system which could be used to simultaneously carry out  
27 combined hydrotreating and hydrocracking to selectively  
28 produce liquid products in the transportation fuels boiling  
29 range.

30

31 Several attempts have been made to provide dual function  
32 combined hydrotreating and hydrocracking processes and  
33 catalyst systems.

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01 U.S. Patent 4,797,196 issued on January 10, 1989 to Kukes  
02 et al. describes a hydrocracking process having intermixed  
03 catalysts. In this process, each of the intermixed  
04 catalysts has hydrodenitritication and/or  
05 hydrodesulfurization activity as well as cracking activity,  
06 that is they both have zeolitic components and function to  
07 crack the feedstock. Thus, although one of the catalysts is  
08 predominantly a hydrotreating catalyst, each catalytic  
09 particle is dual functional.  
10

11 U.S. Patent 4,210,521 issued on July 1, 1980 to Gorring  
12 et al. also describes a dual bed catalytic upgrading process  
13 for refractory hydrocarbon stocks. In this process, the  
14 refractory feedstock is first catalytically hydrotreated and  
15 the hydrotreated product is subsequently cascaded through a  
16 hydrocracking zone. The initial hydrotreating step serves  
17 to convert sulfur and nitrogen derivatives of hydrocarbons  
18 to hydrogen sulfide and ammonia while depositing metal  
19 contaminants.  
20

21 U.S. Patent 4,363,719 issued on December 14, 1982 to  
22 Bousquet et al. describes a process to improve the stability  
23 of a catalyst to be used for lowering the cloud or turbidity  
24 point and the filterability limit temperature of gas-oils.  
25 The catalyst is a composite of a non-acidic  
26 hydrodesulfurization catalyst and a non-zeolitic silica-  
27 alumina based hydroconversion catalyst.  
28

29 It is the principal object of the present invention to  
30 provide a stable catalyst system for combined hydrotreating  
31 and hydrocracking process operations with high selectivity  
32 for liquid products in the transportation fuels boiling  
33 range. This and other objectives are accomplished by the  
34 catalyst system and process summarized below.

## SUMMARY OF THE INVENTION

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In accordance with an aspect of the invention, a dual function catalyst system for combined hydrotreating and hydrocracking process operations comprises two randomly intermixed distinctly different particulate catalysts, the first of which is a hydrodenitritication and/or hydrodesulfurization catalyst having substantially no cracking activity and the second of which is a hydrocracking catalyst, wherein the catalyst particles of both particulate catalysts are substantially the same size, having an effective diameter within a factor of about 4 of each other.

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13  
14

The foregoing catalyst system can be used to carry out combined hydrotreating and hydrocracking processes under typical hydrocracking process conditions.

15  
16

## DETAILED DESCRIPTION OF THE INVENTION

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Those familiar with the art related to the present invention will appreciate the full scope of the catalyst system and the process summarized above and be able to practice the present invention over its full scope from a detailed description of the principal features of the catalyst system and process which follows.

22  
23

### The Catalyst System

24  
25  
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27

The dual function catalyst system of the present invention comprises a randomly intermixed combination of at least two discrete particulate catalysts. The first catalyst is a conventional hydrotreating catalyst of the type used to carry out hydrodenitritication and/or hydrodesulfurization

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01 reactions having substantially no cracking activity. Those  
02 familiar with the art recognize that such catalysts  
03 generally are constituted by a metal from Group VI and a  
04 metal from Group VIII placed on a non-acidic oxide such as  
05 pure alumina. The commercial catalysts generally fall into  
06 one or more of the numerous nickel-molybdenum or cobalt-  
07 molybdenum, or nickel-tungsten, or cobalt-tungsten families.  
08 The catalytic metals are supported by alumina or other low  
09 acidic support material. Such catalysts to be useful in the  
10 present invention do not have cracking activity, that is  
11 they are non-zeolitic non-acidic catalysts which function to  
12 promote hydrodenitritification and/or hydrodesulfurization  
13 reactions. Such catalysts are well known in the art.

14

15 The second catalyst particle is a conventional zeolitic  
16 hydrocracking catalyst of the type used to carry out  
17 hydroconversion reactions to produce transportation fuels.  
18 Those familiar with the art recognize that such catalysts  
19 are generally based on zeolitic materials which may have  
20 been adapted by techniques like ammonia ion exchange and  
21 various forms of calcination. In general, suitable zeolitic  
22 hydrocracking catalysts comprise a hydrogenation component  
23 such as a metal from Group VIB and a metal from Group VIII,  
24 their oxides, their sulfides, and mixtures thereof and an  
25 acidic support of large pore crystalline zeolitic  
26 aluminosilicate.

27

28 One of the zeolites which is considered to be a good  
29 starting material for the manufacture of hydrocracking  
30 catalysts is the well-known synthetic zeolite Y as described  
31 in U.S. Patent 3,130,007 issued April 21, 1964. A number of  
32 modifications to this material have been reported one of  
33 which is ultrastable Y zeolite as described in U.S.  
34 Patent 3,536,605 issued October 27, 1970. To further

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01 enhance the utility of synthetic Y zeolite additional  
02 components can be added. For example, U.S. Patent 3,835,027  
03 issued on September 10, 1974 to Ward et al. describes a  
04 hydrocracking catalysts containing at least one amorphous  
05 refractory oxide, a crystalline zeolitic aluminosilicate and  
06 a hydrogenation component selected from the Group VI and  
07 Group VIII metals and their sulfides and their oxides.

08

09 It has been found that if the two particulate catalysts are  
10 selected so that the effective diameter is substantially the  
11 same for both the hydrotreating and the hydrocracking  
12 catalyst particles it is possible to intermix the two  
13 catalysts to provide a system which surprisingly has the  
14 beneficial attributes of both hydrotreating and  
15 hydrocracking. This is particularly surprising since it is  
16 known that conventional hydrotreating catalysts are rapidly  
17 fouled by coke buildup, and that conventional zeolitic  
18 catalysts catalyze cracking reactions which may cause a heat  
19 increase leading to coke formation at the edges of the  
20 zeolite particle.

21

22 As used herein, the term "intermixed" means that no effort  
23 is made to layer or otherwise segregate the individual  
24 hydrotreating catalyst particles from the individual  
25 hydrocracking catalyst particles. Thus, the hydrotreating  
26 catalyst particles and the hydrocracking catalyst particles  
27 are allowed to physically associate with each other in a  
28 relatively random manner to form a heterogeneous physical  
29 mixture. This can be accomplished prior to or during  
30 catalyst loading.

31

32 In order to provide a catalyst system with intermixed  
33 hydrotreating and hydrocracking particles which is stable  
34 and acceptable for use under conventional hydrocracking

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01 conditions, it has been found that the particle size of each  
02 of the catalytic particles must be substantially the same.  
03 Although there are a number of catalyst sizing conventions,  
04 such as surface to volume ratio, length over diameter ratio,  
05 diameter of the circumscribed circle, etc., when comparing  
06 catalysts which may have nonuniform shape we have chosen to  
07 use the effective diameter of a particle as representative  
08 of its size. As used herein the term "effective diameter"  
09 for a catalyst particle with a circular cross section means  
10 the diameter of that cross section, and for a catalyst  
11 particle with a non-circular cross section means the average  
12 of the major and minor axes. The important aspect of this  
13 parameter is not so much the absolute size of the particles,  
14 but rather the relative size of the hydrotreating catalyst  
15 particles to the size of the hydrocracking catalyst  
16 particles. It is the central feature of the present  
17 invention that for the two intermixed catalysts to form the  
18 catalyst system of this invention the effective diameter of  
19 each must be substantially the same. By "substantially the  
20 same" is meant within a factor of about 4 of each other,  
21 preferably within a factor of about 2 of each other, and  
22 even more preferably within a factor of about 1.5 of each  
23 other.

24

25 Therefore, it is not intended that the present invention  
26 should be limited by the specific size of the catalysts in  
27 question, but rather that the present invention is defined  
28 by the relative size of the particles of the two catalysts.

29

30 It is a principal advantage of the present invention that  
31 since two conventional catalysts are randomly intermixed to  
32 form the catalyst system, it is possible to select a  
33 hydrocracking catalyst which under typical conditions would  
34 be too active, that is, its heat release would be too great

1 for the equipment available, and to reduce that heat release to within  
2 acceptable limitations by combining it with a select hydrotreating catalyst in  
3 proportions which give the desired activity. Those familiar with the art will  
4 recognize that there are an endless variety of such combinations. In general,  
5 the ratio of hydrotreating to hydrocracking catalyst will be within the range of  
6 from about 1:20 to about 20:1, preferably within the range of from about 1:10  
7 to about 10:1, more preferably within the range of from about 1:5 to about 5:1.

8

9 One such combination which has been found to be particularly effective uses  
10 a conventional commercially available nickel-molybdenum hydrotreating  
11 catalyst comprising about 3.1 weight percent nickel and about 16 weight  
12 percent molybdenum with the balance being phosphorous and alumina; and a  
13 Hydrocracking catalyst which is a comulled zeolitic catalyst comprising about  
14 17 weight percent alumina binder, about 12 weight percent molybdenum,  
15 about 4 weight percent nickel, about 30 weight percent  $\gamma$ -zeolite, and about 30  
16 weight percent amorphous silica/alumina. This more general hydrocracking  
17 catalyst comprises a Y zeolite having a unit cell size greater than about 24.55  
18 Angstroms and a crystal size less than about 2.8 microns together with an  
19 amorphous cracking component, a binder, and at least one hydrogenation  
20 component selected from the group consisting of a Group VI metal and/or  
21 Group VIII metal and mixtures thereof.

22

23 In preparing a Y zeolite for use in accordance with the invention herein, the  
24 process as disclosed in U.S. patent

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01 No. 3,808,326 should be followed to produce a Y zeolite  
02 having a crystal size less than about 2.8 microns.

03

04 More specifically, the hydrocracking catalyst suitably  
05 comprises from about 30%-90% by weight of Y zeolite and  
06 amorphous cracking component, and from about 70%-10% by  
07 weight of binder. Preferably, the catalyst comprises rather  
08 high amounts of Y zeolite and amorphous cracking component,  
09 that is, from about 60%-90% by weight of Y zeolite and  
10 amorphous cracking component, and from about 40%-10% by  
11 weight of binder, and being particularly preferred from  
12 about 80%-85% by weight of Y zeolite and amorphous cracking  
13 component, and from about 20%-15% by weight of binder.  
14 Preference is given to the use of silica-alumina as the  
15 amorphous cracking component.

16

17 The amount of Y zeolite in the catalyst ranges from about  
18 5-70% by weight of the combined amount of zeolite and  
19 cracking component. Preferably, the amount of Y zeolite in  
20 the catalyst compositions ranges from about 10%-60% by  
21 weight of the combined amount of zeolite and cracking  
22 component, and most preferably the amount of Y zeolite in  
23 the catalyst compositions ranges from about 15-40% by weight  
24 of the combined amount of zeolite and cracking component.

25

26 Depending on the desired unit cell size, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$   
27 molar ratio of the Y zeolite may have to be adjusted. There  
28 are many techniques described in the art which can be  
29 applied to adjust the unit cell size accordingly. It has  
30 been found that Y zeolites having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio  
31 from about 3 to about 30 can be suitably applied as the  
32 zeolite component of the catalyst compositions according to  
33 the present invention. Preference is given to Y zeolites  
34

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01 having a molar  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio from about 4 to about 12,  
02 and most preferably having a molar  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio from  
03 about 5 to about 8.

04  
05 The amount of cracking component such as silica-alumina in  
06 the hydrocracking catalyst ranges from about 10%-50% by  
07 weight, preferably from about 25%-35% by weight. The amount  
08 of silica in the silica-alumina ranges from about 10%-70% by  
09 weight. Preferably, the amount of silica in the  
10 silica-alumina ranges from about 20%-60% by weight, and most  
11 preferably the amount of silica in the silica-alumina ranges  
12 from about 25%-50% by weight. Also, so-called X-ray  
13 amorphous zeolites (i.e., zeolites having crystallite sizes  
14 too small to be detected by standard X-ray techniques) can  
15 be suitably applied as cracking components according to the  
16 process embodiment of the present invention.

17  
18 The binder(s) present in the hydrocracking catalyst suitably  
19 comprise inorganic oxides. Both amorphous and crystalline  
20 binders can be applied. Examples of suitable binders  
21 comprise silica, alumina, clays and zirconia. Preference is  
22 given to the use of alumina as binder.

23  
24 The amount(s) of hydrogenation component(s) in the catalyst  
25 suitably range from about 0.5% to about 10% by weight of  
26 Group VIII metal component(s) and from about 5% to about 25%  
27 by weight of Group VI metal component(s), calculated as  
28 metal(s) per 100 parts by weight of total catalyst. The  
29 hydrogenation components in the catalyst may be in the  
30 oxidic and/or the sulphidic form. If a combination of at  
31 least a Group VI and a Group VIII metal component is present  
32 as (mixed) oxides, it will be subjected to a sulphiding  
33 treatment prior to proper use in hydrocracking.

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01 Suitably, the catalyst comprises one or more components of  
02 nickel and/or cobalt and one or more components of  
03 molybdenum and/or tungsten or one or more components of  
04 platinum and/or palladium.

05

06 The hydrocracking catalyst comprises from about 3%-10% by  
07 weight of nickel and from about 5%-20% by weight molybdenum.  
08 Preferably, the catalyst comprises from about 4%-8% by  
09 weight of nickel and from about 8%-15% by weight molybdenum,  
10 calculated as metals per 100 parts by weight of total  
11 catalyst.

12

13 The effective diameter of the hydrotreating catalyst  
14 particles was about 0.1 inch, and the effective diameter of  
15 the hydrocracking catalyst particles was also about 0.1  
16 inch. The two catalysts are intermixed in a weight ratio of  
17 about 1.5:1 hydrotreating to hydrocracking catalyst.

18

19 The catalyst system of the present invention can be used in  
20 a variety of configurations. For example, the dual function  
21 system of this invention can be layered with unmixed  
22 hydrotreating and/or hydrocracking catalysts. In a  
23 preferred configuration a single reactor may contain up to  
24 four beds, up to about 60% by volume of the first bed being  
25 unmixed hydrotreating catalyst, from about 10% by volume of  
26 the second bed being the catalyst system of the present  
27 invention, up to about 50% by volume of the third bed being  
28 unmixed hydrocracking catalyst, and up to about 40% by  
29 volume of the fourth bed being unmixed hydrotreating  
30 catalyst.

31

32 Having described in detail the catalyst system which is used  
33 in the process of the present invention, it is appropriate  
34 to consider the second aspect of the present process.

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01

Process Conditions

02

03 The process of the present invention is a combined  
04 hydrotreating and hydrocracking process which comprises  
05 contacting a hydrocarbonaceous feedstock with hydrogen under  
06 typical hydrocracking conditions in the presence of the dual  
07 function catalyst system detailed above.

08

09 Representative feedstocks include petroleum crude oils,  
10 topped or reduced crude oils, solvent deasphalted oils,  
11 distillates, etc. Preferred feedstocks include crude  
12 petroleum and atmospheric and vacuum towered bottoms. These  
13 feedstocks generally have boiling range above about 200°F  
14 and generally have a boiling range between 350°F and about  
15 1050°F. More specifically these feedstocks include heavy  
16 distillates, heavy straight run gas oils and heavy cracked  
17 cycle oils, as well as fluidized catalytic cracking unit  
18 feedstocks.

19

20 The hydrocarbonaceous feedstock is contacted with hydrogen  
21 in the presence of the catalyst system under upgrading  
22 conditions which generally include a temperature in the  
23 range of from about 500°F to about 900°F, preferably between  
24 about 650°F and about 850°F; a pressure of from about 500  
25 pounds per square inch absolute (psia) to about 3,500 psia,  
26 preferably from about 1,000 psia to about 3,000 psia; and a  
27 liquid hourly space velocity (LHSV) of from about 0.1 to  
28 about 6.0, preferably from about 0.5 to about 4; and an oil  
29 to gas ratio of from about 2,000 standard cubic feet per  
30 barrel (scf/bbl) to about 10,000 scf/bbl, preferably from  
31 about 3,000 scf/bbl to about 6,000 scf/bbl.

32

33 With the preferred catalyst system described above it has  
34 been found that preferred process conditions include

1 contacting a hydrocarbonaceous feedstock with hydrogen in the presence of  
2 the physically intermixed catalyst system under hydrocracking conditions  
3 comprising a pressure of about 2,300 psia, a gas to oil ratio at from about  
4 4,000 scf/bbl to about 5,000 scf/bbl, a LHSV of about 1.0, and a temperature  
5 in the range of from about 680°F to about 800°F.

6

7 These and other specific applications of the catalyst system and process of  
8 the present invention are illustrated in the following example.

9

10

### EXAMPLE

11

12 The following Example illustrates the efficacy of the present invention.

13

14 A dual catalyst system was prepared by physically intermixing a commercially  
15 available nickel-molybdenum hydrotreating catalyst comprising about 3.1  
16 weight percent nickel and about 16 weight percent molybdenum with the  
17 balance being phosphorous and alumina; and a zeolitic hydrocracking catalyst  
18 which is a comulled zeolitic catalyst comprising about 17 weight percent  
19 alumina binder, about 12 weight percent molybdenum, about 4 weight percent  
20 nickel, about 30 weight percent Y-zeolite, and about 30 weight percent  
21 amorphous silica/alumina. This hydrocracking catalyst was prepared by the  
22 multi-step process wherein Solution "A" was prepared by dissolving 160.6 g  
23 nickel nitrate hexa hydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] in 70 cc deionized

24

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01 water and then adding about 25 g concentrated nitric acid  
02 (70% HNO<sub>3</sub>).

03

04 Solution "B" was a molybdenum solution prepared by stirring  
05 and filtering a mixture composed of 26.5 weight percent  
06 concentrated aqueous NH<sub>4</sub>OH, 28.9 weight percent MoO<sub>3</sub>,  
07 balance deionized water.

08

09 A solid mixture was prepared by mixing 174.7 grams alumina  
10 powder, 293.8 grams SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> powder, and 303.8 grams ultra  
11 stable Y zeolite powder in a sigma-blade mixer for 5 minutes  
12 at about 150°F mixer jacket temperature. To the solid  
13 mixture was then added about 150 cc of deionized water, and  
14 the mixture mixed an additional 5 minutes. Solution "A" was  
15 then added to the wet solid mixture, and the mixing was  
16 continued for an additional 35 minutes.

17

18 483.1 grams of Solution "B" were then dripped into the wet  
19 solid mixture over a 5-minute period. 70 cc deionized water  
20 were added, and the wet solid mixture was mixed for an  
21 additional 15 minutes.

22

23 The wet mixture was extruded in a 2-inch Bonnot extruder.  
24 The extrudates were dried in a preheated oven at 320°F for  
25 1 hour. They were then heated to 950°F at 288°F/hr in  
26 10 com dry air, held for 1 hour at 950°F, and then cooled to  
27 room temperature.

28

29 The effective diameter of the hydrotreating catalyst  
30 particles was about 0.1 inch, and the effective diameter of  
31 the hydrocracking catalyst particles was also about 0.1  
32 inch. The two catalysts are intermixed in a weight ratio of  
33 about 1.5:1 hydrotreating to hydrocracking catalyst.

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01 A feedstock of heavy gas oil having the following  
02 characteristics was contacted with above dual catalyst  
03 system in the presence of hydrogen:

04  
05 API Gravity - 21.0  
06 Nitrogen - 2520 ppm  
07 Sulfur - 0.8 weight percent  
08 D2887 Simulated Distillation  
09 St - 380°F  
10 50% - 742°F  
11 EP - 952°F  
12

13 The process conditions were maintained as follows:

14  
15 1.0 LHSV  
16 2,300 psig total pressure  
17 5,500 scf/bbl gas rate  
18 680°F-800°F temperature range  
19

20 At a target product composition of 1.0 ppm nitrogen and 10  
21 ppm sulfur, the dual catalyst system resulted in a 17°F  
22 higher activity and 80% improvement in catalyst life  
23 relative to a conventional layered catalyst system  
24 comprising 60 volume percent of a commercial zeolitic  
25 catalyst and 40 volume percent of a commercial nonzeolitic  
26 silica/alumina catalyst.

27  
28 There are numerous variations on the present invention which  
29 are possible in light of the teachings and example  
30 supporting the present invention. It is therefore  
31 understood that within the scope of the following claims,  
32 the invention may be practiced otherwise than as  
33 specifically described or exemplified herein.  
34

**CLAIMS**

1. A dual function catalyst system for combined hydrotreating and hydrocracking process operations comprising two randomly intermixed distinctly different particulate catalysts, the first of which is a hydrodenitrification and/or hydrodesulfurization catalyst having substantially no cracking activity and the second of which is a hydrocracking catalyst, wherein the catalyst particles of both particulate catalysts are substantially the same size, having an effective diameter within a factor of about 4 of each other.
2. A catalyst system according to claim 1, wherein the particulate hydrotreating catalyst comprises a catalyst selected from the group consisting of nickel-molybdenum, cobalt-molybdenum, nickel-tungsten and cobalt-tungsten.
3. A catalyst system according to claim 1, wherein the particulate hydrotreating catalyst comprises nickel-molybdenum.
4. A catalyst system according to claim 3, wherein the hydrotreating catalyst comprises about 3.1 weight percent nickel and about 16 weight percent molybdenum and the balance is phosphorous and alumina.
5. A catalyst system according to claim 1, wherein the hydrocracking catalyst comprises a Y-zeolite.
6. A catalyst system according to claim 5, wherein the hydrocracking catalyst comprises a Y zeolite having a unit cell size greater than about 24.55 Angstroms and a crystal size less than about 2.8 microns together with an amorphous cracking component, a binder, and at least one hydrogenation component selected from the group consisting of a Group VI metal, and/or a Group VIII metal and mixtures thereof.

7. A catalyst system according to claim 6, wherein the hydrocracking catalyst is a comulled zeolitic catalyst comprising about 17 weight percent alumina binder, about 12 weight percent molybdenum, about 4 weight percent nickel, about 30 weight percent Y-zeolite, and about 30 weight percent amorphous silica/alumina.
8. A catalyst system according to claim 7, wherein the hydrotreating catalyst comprises about 3.1 weight percent nickel and about 16 weight percent molybdenum and the balance is phosphorous and alumina.
9. A catalyst system according to claim 1, wherein the hydrotreating catalyst and hydrocracking catalyst have an effective diameter within a factor of about 2 of each other.
10. A catalyst system according to claim 1, wherein the weight ratio of the hydrotreating catalyst to the hydrocracking catalyst is from about 20:1 to about 1:20.
11. A catalyst system according to claim 1, wherein the weight ratio of the hydrotreating catalyst to the hydrocracking catalyst is from about 10:1 to about 1:10.
12. A catalyst system according to claim 1, wherein the weight ratio of the hydrotreating catalyst to the hydrocracking catalyst is from about 5:1 to about 1:5.
13. A catalyst system according to claim 1, wherein the system is layered with an unmixed hydrotreating catalyst.
14. A catalyst system according to claim 1, wherein the system is layered with an unmixed hydrocracking catalyst.