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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Catalysts for Cracking Hydrocarbons

We, W. R. GRACE & CO., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 7 Hanover Square, New York 5, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, ~~and~~ the method by which it is to be performed, to be particularly described in and by the following statement:

THIS INVENTION relates to catalysts for cracking hydro-carbons, especially petroleum.

Silica-alumina fluid cracking catalysts are generally prepared by neutralizing an alkali metal silicate solution with mineral acid, adding alum (i.e. aluminium sulphate) to the resulting hydrogel to incorporate the requisite amount of alumina in the final catalyst and precipitating the alum as alumina by the addition of a suitable base. In addition to the silica-alumina cracking catalysts, other fluid catalysts which have been used in the cracking of hydrocarbons are those prepared by treating certain clays, such as bentonite and montmorillonite, with an acid to improve their cracking characteristics. The catalysts prepared form clay are generally used in systems where price is an important factor. Efforts have been made to decrease the cost of the synthetic silica-alumina fluid cracking catalyst by adding varying amounts of clay to the catalyst in the process of preparation.

Where increased activity and selectivity are desired, these characterisitcs may be imparted to the catalyst by increasing the number of acid sites. This may be done by increasing the alumina concentration, but it has now been discovered that another suitable method is to use commercially available zeolitic alumina-silicates as one of the components of the catalyst. However, the alkali metal ions normally present in the zeolites must be removed prior to use of the catalysts for cracking hydrocarbons in order to realize maximum catalyst activity, selectivity of cracking and structural stability.

According to the invention there is provided a silica-alumina hydrocarbon catalyst containing 10 to 30%, preferably 13 to 25%, by weight of active alumina and a substantial proportion, preferably 10 to 30% by weight of a zeolite having a molar ratio of silica to alumina of at least 2.5 : 1, preferably 2.5 : 1 to 12 : 1, the catalyst being substantially free from alkali metal ions. The presence of alkali metal ions in a hydrocarbon cracking catalyst impairs its efficiency, and by "substantially free from alkali metal ions" is meant that the catalyst should not contain an amount of alkali metal ions which makes the composition unsuitable for use as a hydrocarbon cracking catalyst. The catalyst preferably contains at most the equivalent of 0.5% by weight of sodium oxide.

The invention provides a process for preparing such catalysts by a method in which an alkali metal silicate is converted into silica hydrogel by acidifying an aqueous solution of the silicate, and aluminium sulphate is added to the hydrogel and the aluminum is precipitated as hydrated alumina, which process comprises adding a zeolite in which the molar ratio of silica to alumina is at least 2.5 : 1 to a reaction mixture of the process at any stage in the preparation and, if the zeolite is not substantially free from sodium and other alkali metal ions, treating a reaction mixture of the process in which the zeolite has been incorporated to free it from such ions.

Microselective adsorbents of the zeolite group are crystalline metal alumina-silicates with a three dimensional structure of silica and alumina tetrahedra. The zeolite structure is characterised by a repeating three dimensional network of large open alumino-silicate cages inter-connected by small uni-from openings or pores. Certain of these microselective adsorbents have been prepared synthetically from sodium silicate and sodium

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aluminate. After synthesis, these large cavities are filled with water which can be driven off by heat without collapsing the cage. When dehydrated, these cavities can re-adsorb large quantities of water or other vapours at low partial pressures. Due to the small uniform structures or pore openings connecting the alumino-silicate cages, these zeolites exhibit the unique property of excluding larger molecules from the cavity while allowing smaller molecules to pass through and be adsorbed, thereby acting as microselective adsorbents for molecules according to their size and shape.

Sodium ions or other cations can be removed from zeolites by exchange with other ions, e.g. ammonium ions, hydrogen ions and polyvalent metal cations (for example Mg^{++}, Al^{+++} and rare earth ions), resulting in an increase of the number of acid sites available for cracking hydrocarbons, thereby adding to the total number of acidsites in the composite catalyst. A further advantage of using zeolites is that they help to exclude large ions from the catalyst. These ions, such as polynuclear aromatics, for example, are the classic coke precursors which cause loss of catalytic activity and which are therefore particularly undesirable when adsorbed on cracking sites.

The synthetic microselective adsorbents are available as materials with pore sizes from 2.5 to 15 Angstrom units. Each of these zeolites has a characteristic silica-to-alumina molar ratio. Thus, the zeolite with a 3.5 Angstrom unit pore size has a ~~silea~~-to-alumina ratio of 2 to 1, whereas the zeolite with a 9 to 10 Angstrom unit pore size has a silica to alumina molar ratio of 2.5 to 1. In addition to these synthetic zeolites, certain other compositions are available which have higher silica to alumina ratios. Mordenite, a natural occurring zeolite, for example, contains 12.5 weight percent alumina and has a silica to alumina mole ratio of 10 to 1. It has been found that to be useful in the present invention a zeolite should have the following three characteristics, all of which are found in zeolites having a molar ration of silica to alumina of more than 2.5 : 1. Firstly it should have a robust three dimensional network of silica and alumina tetrahedra in order to withstand the severe thermal and steam environment to which it will be subjected, particularly during regeneration. Secondly, it should be low in alumina and high in silica, since a zeolite in the H^+ or decationized form is more stable if it is low in alumina. Thirdly (and this characteristic is related to the others) it should have a low pore volume and surface area (i.e. a small number of voids and a robust structure); e.g. the pore volume and surface area should be lower than in the zeolites commonly used for adsorption, for which high pore volume and surface area are desirable qualities.

If one of the zeolites commonly used in adsorption processes is used to prepare a silica-alumina catalyst, the more open structure of the zeolite and the high alumina content results in a ~~catalysts~~ which tends to be unstable under extreme thermal conditions. An ideal zeolite for use in cracking catalysts is one which is composed of thicker walled pores, which in turn means a zeolite with a lower total pore volume and surface area. However, the zeolite should have a pore mouth diameter sufficient to admit petroleum feed stock components capable of being selectively cracked to valuable hydrocarbons of the gasoline type hydrocarbons while ~~excluding~~ coke precursors such as polynuclear aromatics; for this reason zeolites having pore openings greater than 3.5 Angstrom units are preferred. Particularly suitable catalysts for use in the present invention are natural and synthetic faujesite, mordenite and erionite. Natural faujesite has pore openings of about 10 Å, cage diameter of 13 Å and a silica to alumina ratio of from 4 : 1 to 6 : 1. Mordenite has a silica to alumina ratio of 8 : 1 to 11 : 1 and has a smaller total pore volume and lower surface area. Erionite has a silica to alumina ratio of 4 : 1 to 7 : 1. An example of another zeolite is that zeolite which has a silica to alumina weight ~~ration~~ of 5 : 1 to 10 : 1 and the empirical formula, $M_2O.Al_2O_3.2\text{-}10.SiO_2$ wherein M can be any one of several different cations or a mixture of cations. This material is hereinafter referred to as Z-16 zeolite.

A preferred process for preparing the new catalysts comprises (1) acidifying a solution of an alkali metal silicate having a weight ratio of silica to alkali metal oxide of 3 : 1 to 3.4 : 1 with carbon dioxide or a mineral acid until a silica hydrogel is formed; (2) adding a solution of aluminium sulphate in an amount sufficient to provide 10 to 30% by weight of active alumina in the final catalyst; (3) when necessary, adding an alkali to precipitate substantially all the aluminium as hydrated alumina; and (4) separating the solids from the resulting mixture. It is necessary to use a base, e.g. ammonia, to precipitate the aluminium in step (3) when a mineral acid has been used in step (1) and also when carbon dioxide has been used in step (1) if if the amount of aluminium sulphate added corresponds to an alumina concentration in the final catalyst above about 15%. The zeolite is added at some stage in the above process; for example it can be added to alkali metal silicate solution before it is gelled; or it can be added as a slurry with the aluminium sulphate (which is preferably added in an amount sufficient to provide 13 to 25% alumina in the final catalyst); or the solids separated in step (4) can be reslurried in water and the zeolite mixed into the slurry, from which the solids mixture is recovered. It is usually convenient to reslurry in water

the solids separated in step (4) and, optionally after addition of zeolite as described above, to spray dry the slurry, and to wash and then re-dry the spray-dried product to prepare the final catalyst.

To remove alkali metal ions from the zeolite, it can be treated with a solution of a compound which replaces sodium and other alkali metal ions in the zeolite with hydrogen ions, ammonium ions or divalent or trivalent metal ions, preferably a solution of mixed rare earth chlorides. The final ~~catalysts~~ preferably contains 1.5 to 15% by weight of rare earths, cerium, lanthanum, neodymium, pracsodymium, samarium and gadolinium. Preferably at least 90%, especially at least 98% of the alkali metal ions in the zeolite, are replaced.

The replacement of the alkali metal ions in the zeolite can be accomplished by conventional exchange techniques. The point at which this base exchange takes place depends, to some extent, on when the zeolite is added to the catalyst mass. If the zeolite is added to the sodium silicate solution before gelation, for example, it may be desirable to have the zeolite in the sodium form since it is being added to a strongly alkaline solution. If the zeolite is added to the alum solution, the possibility of a preferential exchange of the rare earth or other ion in the zeolite with the sodium present as the gelled sodium silicate or with Al^{+++} is an important consideration. This exchange would, of course, result in a loss of the cation values from the catalyst. For that reason, it is usually preferred that the zeolite be in the sodium form if it is added to the alum solution. If the exchanged zeolite is added to a spray drier feed, there is less danger of loss of the base exchanged cation values from the catalyst. In this case, it would be satisfactory to use a zeolite material that had been converted to the desirable form. However, in cases where a catalyst with a reduced polyvalent ion content is desirable, the catalyst can be prepared by adding the exchanged zeolite to the alum solution or to the sodium silicate solution.

For purposes of simplicity, the invention will be described using the commercially available 13% silica-alumina cracking catalyst as the basic material. It is to be understood, however, that the invention is equally applicable to other types of fluid cracking catalysts, the 25% silica-alumina cracking catalysts, and the so-called semi-synthetic cracking catalyst where the silica-alumina cracking ~~catalysts~~ is diluted with clay. Clay may be added to the catalyst at some stage during its preparation.

Briefly summarizing the processing steps in a typical preparation according to this invention, concentrated sodium silicate with a weight ratio of SiO_2 to Na_2O of about 3.25 to 1 is diluted with water to an SiO_2 content of 3 to 8 percent and preferably 4 to 5 percent. The silica is gelled with sulphuric acid or with carbon dioxide at any temperature up to 74°C., preferably 38-57°C. A predetermined amount of microselective zeolite adsorbent may or may not have been added to the sodium silicate. Following gelation, a normal aluminium sulphate solution is added to the gelled sodium silicate. When the silicate is gelled with carbon dioxide, the concentration of the alum solution is such that the sulphate ion thus introduced is usually sufficient to neutralize all the alkali originating from the sodium silicate which has been converted by carbon dioxide to sodium carbonate. Gaseous carbon dioxide released from the system by this sulphate ion can be recovered and recycled for gelation of further sodium silicate.

Following the alumina precipation, the silica-alumina constituents are then removed from the slurry by filtration. The filter cake is then reslurried with a minimum quantity of water to form a slurry of maximum silica-alumina content for spray drying. In an alternative process, the microselective zeolite may be added to the spray drier feed at this step of the process.

After the product has been spray dried, it is generally wet collected with water, washed free of sodium and sulphate impurities and finally flash dried. The order of washing and drying may be varied if desired. The filtered material may be washed prior to drying. The washed material is then spray dried to form silica-alumina microspheres. Washing is preferably carried out with heated dilute ammonium sulphate solution followed by a rinse with heated deionized water.

The catalytic cracking activity, stability and selectivity of the catalyst product can be determined as follows. A sample of catalyst is compressed into pellets and the pellets are deactivated as described below.

A total of 200 ml. of deactivated catalyst is then placed in a reactor and maintained at a temperature of 455°C. During a period of 2 hours, 283.2 ml. of virgin East Texas light gas oil is passed through the hot catalyst and the cracked products are recovered and separated. The fraction which distils below 205°C. as well as any loss are determined and designated distillate plus loss, or more simply D+L. The gas and carbon produced by the catalyst in the cracking test is also determined. These values are designated as gas producing factor and carbon producing factor, or more simply G.P.F. and C.P.F., and are the relative amounts of gas and carbon produced by the present catalyst as compared with a standard reference catalyst of the same activity level. This method is described in "Petroleum Refiner" Volume 31, June, 1952, pages 92 to 100.

The three commonest deactivation procedures are:—

(a) heating for 5 hours at 205°C., then for 3 hours at 565°C. and then for 24 hours in steam at 4.2 kg./cm² and 565°C.;

(b) heating for 5 hours at 205°C., then for 3 hours at 540°C., and finally for 3 hours at 845°C.

(c) heating for 5 hours at 205°C., then for 3 hours at 540°C., and finally for 3 hours at 925°C.

This invention is illustrated by the following Examples, in which parts and percentages are by weight except where otherwise stated.

EXAMPLE 1

To a tank equipped with a stirrer and centrifugal pump were added 76 litres of a sodium silicate solution at 57°C., containing the equivalent of 15.8 g/l of Na_2O and 55.5 g/l of SiO_2, and 2,100 grams of a zeolite containing about 49% SiO_2, 32% Al_2O_3 and 19% Na_2O. The silicate solution and zeolite were circulated through the centrifugal pump for about 10 minutes. Carbon dioxide was then bubbled through the mixture until gelation of the sodium silicate began at a pH of 9.9 and for a further 15 minutes thereafter, at the end of which time the pH of the slurry was 9.6. The gel was aged for 1 hour at 57°C. 6465 grams of an alum solution containing the equivalent of 96 g/l of Al_2O_3 and having a ratio of sulphate to alumina of 3:1 were then added, followed by dilute sulphuric acid until the pH was 5.6. The slurry was mixed for 15 minutes and then filtered. The filter cake was reslurried with water at a pH of 6. The very viscous slurry obtained from this operation was fed to a spray dryer. The density of the spray dried product was 0.74 g/cc.

The product was then treated successively with six portions, each of 9.5 litres, of a 2% solution of rare earth chlorides, with filtration of the product between each treatment. The product was treated for 2.5 hours each with the first and second portions, for 17 hours with the third portion, for 2.5 hours each with the fourth and fifth portions and for 48 hours with the sixth portion. After this ion exchange treatment, which removed about 89% of the sodium ions, the product was washed with distilled water and air dried. The chemical composition of the product is shown in Table 1 below.

EXAMPLE II

For purposes of comparison, Example I was repeated up to the spray drying stage, except that the zeolite was omitted and the sodium silicate solution contained 16.83 g/l of Na_2O and 55.5 g/l of SiO_2. The spray dried product, which had a density of 0.79 g/cc., was washed first with four 23 litre washes of 2°Bé ammonium sulphate solution at room ~~teperature~~ and a pH of 5.6 and then with three washes of distilled water adjusted to a pH of 8.6. The chemical composition of the product is shown in Table 1 below.

EXAMPLE III

To a tank equipped with a stirrer and centrifugal pump were added 76 litres of a sodium silicate solution at 57°C, containing the equivalent of 16.84 g/l of Na_2O and 55.5 g/l of SiO_2, and 1965 grams of a zeolite containing 66% SiO_2, 22% Al_2O_3 and 12% Na_2O. The silicate solution and zeolite were circulated through the centrifugal pump for about 10 minutes. Carbon dioxide was then bubbled through the mixture for about 22 minutes, then the pH was 9.6. The gel was aged for 1 hour at 57°C. 3,100 grams of an alum solution containing the equivalent of 96 g/l of Al_2O_3 were then added, reducing the pH to about 8.1. The mixture was agitated for about 10 minutes and then filtered. The filter cake was reslurried with 5.5 litres of water and spray dried. The spray dried product was then treated (as in Example I) successively with six portions, each of 9.5 litres, of a 2% solution of rare earth chlorides, with filtration of the product between each treatment. The product was treated for periods of 2.5, 2.5, 17, 2.5, 2.5 and 48 hours respectively with the six portions. After this ion exchange treatment, which removed about 83% of the sodium ions, the product was filtered, washed with distilled water until free of chloride ion and air dried. The weight ratio of silica to alumina in the product was 6.7:1. The chemical composition of the product is shown in Table 1 below.

EXAMPLE IV

Example I was repeated except that the treatment with the solution of the rare earth chlorides was continued until about 97% of the sodium ions had been removed. The chemical composition of the product is shown in Table 1 below.

EXAMPLE V

Catalyst A was prepared according to the procedure of Example I and catalyst B by the same procedure except that the zeolite was subjected to ion exchange treatment with a solution of rare earth chlorides before being added to sodium silicate solution. The

chemical compositions of catalysts A and B are shown in Table I below.

TABLE I

Chemical composition in percentages by weight.

Ex. No.	Zeolite	Rare Earth Oxides	Na_2O	Al_2O_3
I	25	11.0	0.56	18.03
II	0	0		14.4
III	25	7.4	0.56	
IV	25	9.6	0.14	
V A	25	4.9	0.16	
V B	25	9.6	0.14	

Various properties of the catalysts prepared in Examples I to V were determined, and the results are tabulated below. Table II shows the surface area (S.A) in m^2/g, pore volume (PV) in cc/g and pore diameter (PD) in Angstrom units, after heating the catalyst in air for the times and at the temperature shown. Tables III and IV show the surface area and pore volume after heating first in steam and then in air for the times and at the temperatures and pressures shown. Table V shows the distillate plus loss (D+L) values, the gas producing factors (GPF) and carbon producing factors (CPF) after deactivation in accordance with procedures (b) and (c) above. Table VI shows the results of using the catalysts prepared in Examples I and II, after they had been treated with steam at 665°C at atmospheric pressure for 20 hours, to treat West Texas heavy gas oil, at a cracking temperature of 490°C, a catalyst to oil weight ratio of 4:1 and a weight hourly space velocity of 26. Table VI shows the volume percent conversion of the feed, the percent volume of gasoline (C_5+) produced and the coke yield in weight per cent.

TABLE II

	3 Hrs at 540°C		3 Hrs at 675°C		3 Hrs at 845°C			3 Hrs at 925°C		
	SA	PV	SA	PV	SA	PV	PD	SA	PV	PD
Ex I	472	0.73	441	0.68	333	0.52	62	37	0.07	75
Ex II	459	0.74			354	0.66	74	263	0.44	66
Ex III			462	0.80	432	0.70				
Ex IV			402	0.67						
Ex VA			425	0.71						
Ex VB			402	0.67						

TABLE III

	Treatment with steam at 665°C. at atmospheric pressure for 20 hours, followed by heating for:—							
	NONE		3 Hrs at 845°C		3 Hrs at 900°C		3 Hrs at 925°C	
	SA	PV	SA	PV	SA	PV	SA	PV
Ex I	256	0.56	232	0.55	130	0.35	56	0.15
Ex IV	295	0.66	272	0.62	212	0.55	141	0.44
Ex VA			197	0.57	156	0.45	142	0.45
Ex VB			272	0.62	212	0.55	141	0.44

TABLE IV

Treatment with steam for 24 hours at 565°C and 4.2 kg/cm², followed by heating for:—						
	NONE		3 Hrs at 730°C		3 Hrs at 790°C	
	SA	PV	SA	PV	SA	PV
Ex I	218	0.61				
Ex II	175	0.46				
Ex VA			210	0.59	205	0.57
Ex VB			277	0.61	~~187~~	0.63

TABLE V

	Properties after deactivation according to:—					
	PROCEDURE (b)			PROCEDURE (c)		
	D+L	GPF	CPF	D+L	GPF	CPF
Ex I	46.9	1.11	1.13	7.6	1.76	2.13
Ex II	49.5	1.00	0.98	47.0	0.94	0.93

TABLE VI

	% Conversion	~~C~~ + Prod'n	% Coke Yield
Ex I	85	70	6.5
Ex II	56	46	3

A comparison of the figures of Table VI shows clearly the improvement in performance as a cracking catalyst which results from the incorporation of a zeolite into the catalyst. On the other hand Tables II and V show that the catalyst of Example I undergoes virtually complete collapse of the structure and loss of activity after prolonged treatment at 925°C., and that it is therefore unsatisfactory for use at such temperatures, which may be employed in commercial operation. The use of a zeolite having a higher ratio of silica to alumina results in a catalyst which not only has a higher initial surface area and pore volume, but is also more resistant to change when heated at high temperatures. Thus the surface area of the catalyst of Example I after heating at 845°C. for 3 hours is 108 m^2/g less than after heating at 675°C. for 3 hours, whereas the surface area of the catalyst of Example III is only 30 m^2/g less.

The sodium oxide contents of the catalysts of Examples I and III (0.56%) are somewhat higher than is preferred, and the Tables show that the catalysts of Examples IV and V, which contain less sodium oxide, have much better thermal stability.

A comparison of the data for Examples VA and VB shows that a catalyst in which the zeolite is subjected to ion exchange treatment before rather than after it is added to the sodium silicate shows a gain or negligible loss of surface area on heating at 790°C. and 845°C., and the performance at lower temperatures offsets the rather greater loss of surface area at higher temperatures of 900°C. and 925°C. so that the surface area of catalyst B is generally greater on heating than the surface area of catalyst A.

The general procedure of Example III can be followed when the zeolite is added as a slurry with the aluminium sulphate, or to the slurry of the filter cake in water, immediately before spray drying. If desired the zeolite can be treated with the solution of rare earth chlorides before it is added and the treatment of the final product with a solution of rare earth chlorides can then be omitted. Preferably at least 98% of the sodium is removed from the zeolite.

WHAT WE CLAIM IS:

1. A process for preparing a silica-alumina hydrocarbon cracking catalyst by a method in which an alkali metal silicate is converted into silica hydrogel by acidifying an aqueous solution of the silicate, and aluminium sulphate is added to the hydrogel and the aluminium is precipitated as hydrated alumina, which process comprises adding a zeolite in which the molar ratio of silica to alumina is at least 2.5:1 to a reaction mixture of the process at any stage in the preparation and, if the zeolite is not substantially free from sodium and other alkali metal ions, treating a reaction mixture of the process in which the zeolite has been incorporated to free it from such ions.

2. Process according to claim 1 which comprises (1) acidifying a solution of an alkali metal silicate having a weight ratio of silica to alkali metal oxide of 3:1 to 3.4:1 with carbon dioxide or a mineral acid until a silica hydrogel is formed; (2) adding a solution of aluminium sulphate in an amount sufficient to provide 10 to 30% by weight of active alumina in the final catalyst; (3) when a mineral acid has been used in step (1), and when necessary when carbon dioxide has been used in step (1), adding an alkali to precipitate substantially all the aluminium as hydrated alumina; and (4) separating the solids from the resulting mixture.

3. Process according to claim 2 wherein sufficient aluminium sulphate is added to provide 13 to 25% by weight of alumina in the final catalyst.

4. Process according to any one of the preceding claims wherein the zeolite is added to the alkali metal silicate solution before it is gelled.

5. Process according to any one of claims 1 to 4, wherein the zeolite is added to the hydrogel as a slurry with the aluminium sulphate solution.

6. Process according to any one of claims 2 to 5 wherein the solids separated in step (4) are reslurried in water and spray dried.

7. Process according to Claim 2 or 3 wherein the solids separated in step (4) are reslurried in water and the zeolite is added to the slurry, and after mixing the zeolite and the solids, the mixture is spray dried to recover the catalyst.

8. Process according to any one of the preceding claims wherein the zeolite has been treated before it is incorporated in a mixture of the process or the mixture containing the zeolite is treated, with a solution of a compound which replaces sodium and other alkali metal ions in the zeolite with hydrogen ions, ammonium ions or divalent or trivalent metal ions.

9. Process according to Claim 8 wherein the zeolite has been, or is, treated with a solution of mixed rare earth chlorides.

10. Process according to Claim 9 wherein the final catalyst contains 1.5 to 15% by weight of rare earths.

11. Process according to any one of Claims 8 to 10 wherein at least 90% of the sodium and other alkali metal ions in the zeolite are replaced.

12. Process according to Claim 11 wherein at least 98% of sodium and other alkali metal ions are replaced.

13. Process according to any one of the preceding claims wherein sufficient zeolite is added to provide 10 to 30% by weight of zeolite in the final catalyst.

14. Process according to any one of the

A comparison of the figures of Table VI shows clearly the improvement in performance as a cracking catalyst which results from the incorporation of a zeolite into the catalyst. On the other hand Tables II and V show that the catalyst of Example I undergoes virtually complete collapse of the structure and loss of activity after prolonged treatment at 925°C., and that it is therefore unsatisfactory for use at such temperatures, which may be employed in commercial operation. The use of a zeolite having a higher ratio of silica to alumina results in a catalyst which not only has a higher initial surface area and pore volume, but is also more resistant to change when heated at high temperatures. Thus the surface area of the catalyst of Example I after heating at 845°C. for 3 hours is 108 m^2/g less than after heating at 675°C. for 3 hours, whereas the surface area of the catalyst of Example III is only 30 m^2/g less.

The sodium oxide contents of the catalysts of Examples I and III (0.56%) are somewhat higher than is preferred, and the Tables show that the catalysts of Examples IV and V, which contain less sodium oxide, have much better thermal stability.

A comparison of the data for Examples VA and VB shows that a catalyst in which the zeolite is subjected to ion exchange treatment before rather than after it is added to the sodium silicate shows a gain or negligible loss of surface area on heating at 790°C. and 845°C., and the performance at lower temperatures offsets the rather greater loss of surface area at higher temperatures of 900°C. and 925°C. so that the surface area of catalyst B is generally greater on heating than the surface area of catalyst A.

The general procedure of Example III can be followed when the zeolite is added as a slurry with the aluminium sulphate, or to the slurry of the filter cake in water, immediately before spray drying. If desired the zeolite can be treated with the solution of rare earth chlorides before it is added and the treatment of the final product with a solution of rare earth chlorides can then be omitted. Preferably at least 98% of the sodium is removed from the zeolite.

WHAT WE CLAIM IS:

1. A process for preparing a silica-alumina hydrocarbon cracking catalyst by a method in which an alkali metal silicate is converted into silica hydrogel by acidifying an aqueous solution of the silicate, and aluminium sulphate is added to the hydrogel and the aluminium is precipitated as hydrated alumina, which process comprises adding a zeolite in which the molar ratio of silica to alumina is at least 2.5:1 to a reaction mixture of the process at any stage in the preparation and, if the zeolite is not substantially free from sodium and other alkali metal ions, treating a reaction mixture of the process in which the zeolite has been incorporated to free it from such ions.

2. Process according to claim 1 which comprises (1) acidifying a solution of an alkali metal silicate having a weight ratio of silica to alkali metal oxide of 3:1 to 3.4:1 with carbon dioxide or a mineral acid until a silica hydrogel is formed; (2) adding a solution of aluminium sulphate in an amount sufficient to provide 10 to 30% by weight of active alumina in the final catalyst; (3) when a mineral acid has been used in step (1), and when necessary when carbon dioxide has been used in step (1), adding an alkali to precipitate substantially all the aluminium as hydrated alumina; and (4) separating the solids from the resulting mixture.

3. Process according to claim 2 wherein sufficient aluminium sulphate is added to provide 13 to 25% by weight of alumina in the final catalyst.

4. Process according to any one of the preceding claims wherein the zeolite is added to the alkali metal silicate solution before it is gelled.

5. Process according to any one of claims 1 to 4, wherein the zeolite is added to the hydrogel as a slurry with the aluminium sulphate solution.

6. Process according to any one of claims 2 to 5 wherein the solids separated in step (4) are reslurried in water and spray dried.

7. Process according to Claim 2 or 3 wherein the solids separated in step (4) are reslurried in water and the zeolite is added to the slurry, and after mixing the zeolite and the solids, the mixture is spray dried to recover the catalyst.

8. Process according to any one of the preceding claims wherein the zeolite has been treated before it is incorporated in a mixture of the process or the mixture containing the zeolite is treated, with a solution of a compound which replaces sodium and other alkali metal ions in the zeolite with hydrogen ions, ammonium ions or divalent or trivalent metal ions.

9. Process according to Claim 8 wherein the zeolite has been, or is, treated with a solution of mixed rare earth chlorides.

10. Process according to Claim 9 wherein the final catalyst contains 1.5 to 15% by weight of rare earths.

11. Process according to any one of Claims 8 to 10 wherein at least 90% of the sodium and other alkali metal ions in the zeolite are replaced.

12. Process according to Claim 11 wherein at least 98% of sodium and other alkali metal ions are replaced.

13. Process according to any one of the preceding claims wherein sufficient zeolite is added to provide 10 to 30% by weight of zeolite in the final catalyst.

14. Process according to any one of the

preceding claims wherein the zeolite has a molar ratio of silica to alumina of 2.5:1 to 12:1.

15. Process according to Claim 14 wherein the zeolite is a natural or synthetic faujesite, mordenite or erionite.

16. Process according to any one of the preceding claims wherein clay is added to the catalyst at some stage during its preparation.

17. Process for the preparation of a silica-alumina hydrocarbon catalyst containing a zeolite substantially as described.

18. Silica-alumina hydrocarbon cracking catalysts prepared by the process of any one of the preceding claims.

19. A silica-alumina hydrocarbon cracking catalyst containing 10 to 30%, preferably 13 to 25%, by weight of active alumina and 5—30%, of a zeolite having a molar ratio of silica to alumina of at least 2.5:1, the catalyst being substantially free from alkali metal ions.

20. A silica-alumina catalyst according to Claim 19 in which the zeolite has a molar ratio of silica to alumina of 2.5:1 to 12:1.

21. A silica-alumina catalyst according to Claim 19 or 20 containing the equivalent of at most 0.5% by weight of sodium oxide.

22. A catalyst according to Claim 20 or 21 containing 10 to 30% by weight of the zeolite.

23. A catalyst according to any one of Claims 20 to 22 wherein at least some of the cations in the zeolite are rare earths.

24. A catalyst according to Claim 23 containing 1.5 to 15% by weight of rare earths.

25. A catalyst according to any one of Claims 20 to 24 wherein the zeolite is a natural or synthetic faujesite, mordenite or erionite.

26. A catalyst according to Claim 20 substantially as described.

27. Process for cracking hydrocarbons which comprises contacting the hydrocarbons under cracking conditions with a catalyst as claimed in any one of Claims 18 to 26.

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