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(54) Title: LAYERED CATALYST COMPOSITION AND PROCESSES FOR PREPARING AND USING THE
COMPOSITION

(57) **Abrégé/Abstract:**

This invention relates to a layered catalyst composition, a process for preparing the composition and processes for using the composition. The catalyst composition comprises an inner core such as alpha-alumina, and an outer layer bonded to the inner core composed of an outer refractory inorganic oxide such as gamma-alumina. The outer layer optionally has uniformly dispersed thereon a platinum group metal such as platinum and a promoter metal such as tin. The composition also optionally contains a modifier metal such as lithium. The catalyst composition shows improved durability and selectivity for dehydrogenating hydrocarbons.

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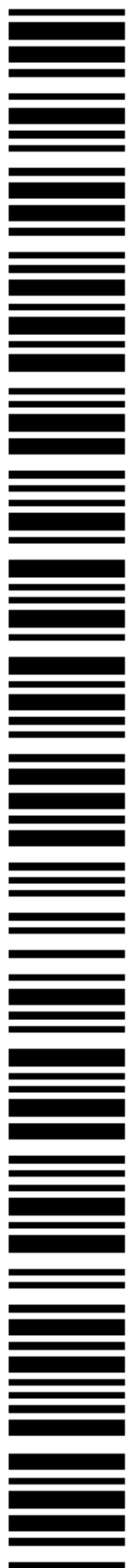
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(54) Title: LAYERED CATALYST COMPOSITION AND PROCESSES FOR PREPARING AND USING THE COMPOSITION

(57) Abstract: This invention relates to a layered catalyst composition, a process for preparing the composition and processes for using the composition. The catalyst composition comprises an inner core such as alpha-alumina, and an outer layer bonded to the inner core composed of an outer refractory inorganic oxide such as gamma-alumina. The outer layer optionally has uniformly dispersed thereon a platinum group metal such as platinum and a promoter metal such as tin. The composition also optionally contains a modifier metal such as lithium. The catalyst composition shows improved durability and selectivity for dehydrogenating hydrocarbons.



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"LAYERED CATALYST COMPOSITION AND PROCESSES
FOR PREPARING AND USING THE COMPOSITION"

BACKGROUND OF THE INVENTION

Hydrocarbon conversion processes are carried out using catalysts including zeolites and supports containing catalytic components. Platinum based catalysts with or without promoters and modifiers are commonly used. One such hydrocarbon conversion process is the dehydrogenation of hydrocarbons, particularly alkanes such as isobutane, which are converted to isobutylene. For example, US-A-3,878,131 (and related US-A-3,632,503 and US-A-3,755,481) discloses a catalyst comprising a platinum metal, a tin oxide component and a germanium oxide component. All components are uniformly dispersed throughout the alumina support. US-A-3,761,531 (and related US-A-3,682,838) discloses a catalytic composite comprising a platinum group component, a Group IVA metallic component, e.g., germanium, a Group VA metallic component, e.g., arsenic, antimony and an alkali or alkaline earth component all dispersed on an alumina carrier material. Again all the components are evenly distributed on the carrier.

US-A-3,558,477, US-A-3,562,147, US-A-3,584,060 and US-A-3,649,566 all disclose catalytic composites comprising a platinum group component and a rhenium component on a refractory oxide support. However, as before, these references disclose that the best results are achieved when the platinum group component and rhenium component are uniformly distributed throughout the catalyst.

It is also known that for certain processes selectivity towards desirable products is inhibited by excessive residence time of the feed or the products at the active sites of the catalyst. Thus, US-A-4,716,143 describes a catalyst in which the platinum group metal is deposited in an outer layer (400 μm) of the support. No preference is given to how the modifier metal should be distributed throughout the support. Similarly US-A-4,786,625 discloses a catalyst in which the platinum is deposited on the surface of the support whereas the modifier

metal is evenly distributed throughout the support.

US-A-3,897,368 describes a method for the production of a noble metal catalyst where the noble metal is platinum and the platinum is deposited selectively upon the external surface of the catalyst. However, this disclosure describes the advantages of impregnating only platinum on the exterior layer and utilizes a specific type of surfactant to achieve the surface impregnation of the noble metal.

The art also discloses several references where a catalyst contains an inner core and an outer layer or shell. For example, US-A-3,145,183 discloses spheres having an impervious center and a porous shell. Although it is disclosed that the impervious center can be small, the overall diameter is 1/8" or larger. It is stated that for smaller diameter spheres (less than 1/8"), uniformity is hard to control. US-A-5,516,740 discloses a thin outer shell of catalytic material bonded to an inner core of catalytically inert material. The outer core can have catalytic metals such as platinum dispersed on it. US 5,516,740 further discloses that this catalyst is used in an isomerization process. Finally, the outer layer material contains the catalytic metal prior to it being coated onto the inner core.

US-A-4,077,912 and US-A-4,255,253 disclose a catalyst having a base support having deposited thereon a layer of a catalytic metal oxide or a combination of a catalytic metal oxide and an oxide support. WO98/14274 discloses a catalyst which comprises a catalytically inert core material on which is deposited and bonded a thin shell of material containing active sites.

Applicants have developed a layered catalyst composition which differs from the prior art in several ways. The composition comprises an inner core such as alpha alumina and an outer layer such as gamma alumina or a zeolite. The outer layer optionally has uniformly distributed thereon at least one platinum group metal such as platinum and a modifier metal such as tin. The platinum group metal to modifier metal atomic ratio varies from 0.1 to 5. The outer layer

has a thickness of 40 to 400 microns. A modifier metal, e.g., lithium, can also optionally be present on the catalyst composition and may be present either entirely in the layer or distributed throughout the catalyst composition. Finally, the composition is prepared using an organic bonding agent such as polyvinyl alcohol which increases the bond between the layer and the inner core thereby reducing loss of the layer by attrition.

SUMMARY OF THE INVENTION

The present invention relates to a layered catalyst composition, a process for preparing the composition and hydrocarbon conversion processes using the composition. One embodiment is a layered catalyst composition comprising an inner core, an outer layer bonded to said inner core, the outer layer comprising an outer refractory inorganic oxide optionally having uniformly dispersed thereon at least one platinum group metal, optionally a promoter metal and the catalyst composition further optionally having dispersed thereon a modifier metal and where the inner core is selected from the group consisting of alpha alumina, theta alumina, silicon carbide, metals, cordierite, zirconia, titania and mixtures thereof.

Another embodiment of the invention is a hydrocarbon conversion process comprising contacting a hydrocarbon fraction with the layered composition described above under hydrocarbon conversion conditions to give a converted product.

Another hydrocarbon conversion process is the alkylation of aromatic hydrocarbons using a layered composition comprising an inner core and an outer layer comprising a zeolite and a binder.

A still further embodiment of the invention is a process for preparing the layered catalyst composition described above, the process comprising:

- a) coating an inner core with a slurry comprising the outer refractory inorganic oxide and an organic bonding agent, said outer oxide having

uniformly dispersed thereon at least one promoter metal, drying the coated core and calcining at a temperature of 400°C to 900°C for a time sufficient to bond the outer layer to the inner core and provide a layered composition.

These and other objects and embodiments will become more clear after a detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The layered catalyst composition comprises an inner core composed of a material which has substantially lower adsorptive capacity for catalytic metal precursors, relative to the outer layer. Some of the inner core materials are also not substantially penetrated by liquids, e.g., metals. Examples of the inner core material include, but are not limited to, refractory inorganic oxides, silicon carbide and metals. Examples of refractory inorganic oxides include without limitation alpha alumina, theta alumina, cordierite, zirconia, titania and mixtures thereof. A preferred inorganic oxide is alpha alumina.

These materials which form the inner core can be formed into a variety of shapes such as pellets, extrudates, spheres or irregularly shaped particles although not all materials can be formed into each shape. Preparation of the inner core can be done by means known in the art such as oil dropping, pressure molding, metal forming, pelletizing, granulation, extrusion, rolling methods and marumerizing. A spherical inner core is preferred. The inner core whether spherical or not has an effective diameter of 0.05 mm to 5 mm and preferably from 0.8 mm to 3 mm. For a non-spherical inner core, effective diameter is defined as the diameter the shaped article would have if it were molded into a sphere. Once the inner core is prepared, it is calcined at a temperature of 400°C to 1500°C.

The inner core is now coated with a layer of a refractory inorganic oxide which is different from the inorganic oxide which may be used as the inner core and will be referred to as the outer refractory inorganic oxide. This outer

refractory oxide is one which has good porosity, has a surface area of at least $20\text{m}^2/\text{g}$, and preferably at least $50\text{m}^2/\text{g}$, an apparent bulk density of 0.2g/ml to 1.0g/ml and is chosen from the group consisting of gamma alumina, delta alumina, eta alumina, theta alumina, silica/alumina, zeolites, non-zeolitic molecular sieves (NZMS), titania, zirconia and mixtures thereof. It should be pointed out that silica/alumina is not a physical mixture of silica and alumina but means an acidic and amorphous material that has been cogelled or coprecipitated. This term is well known in the art, see e.g., U.S.-A-3,909,450; 3,274,124 and 4,988,659. Examples of zeolites include, but are not limited to, zeolite Y, zeolite X, zeolite L, zeolite beta, ferrierite, MFI, mordenite and erionite. Non-zeolitic molecular sieves (NZMS) are those molecular sieves which contain elements other than aluminum and silicon and include silicoaluminophosphates (SAPOs) described in U.S.-A-4,440,871, ELAPOs described in U.S.-A-4,793,984, MeAPOs described in U.S.-A- 4,567,029. Preferred refractory inorganic oxides are gamma and eta alumina.

A preferred way of preparing a gamma alumina is by the well-known oil drop method which is described in U. S-A- 2, 620,314. The oil drop method comprises forming an aluminum hydrosol by any of the techniques taught in the art and preferably by reacting aluminum metal with hydrochloric acid; combining the hydrosol with a suitable gelling agent, e. g., hexamethylenetetraamine; and dropping the resultant mixture into an oil bath maintained at elevated temperatures (93°C). The droplets of the mixture remain in the oil bath until they set and form hydrogel spheres. The spheres are then continuously withdrawn from the oil bath and typically subjected to specific aging and drying treatments in oil and ammoniacal solutions to further improve their physical characteristics. The resulting aged and gelled spheres are then washed and dried at a relatively low temperature of 80°C to 260°C and then calcined at a temperature of 455° to 705°C for a period of 1 to 20 hours. This treatment effects conversion of the hydrogel to the corresponding crystalline gamma alumina.

The layer is applied by forming a slurry of the outer refractory oxide and then coating the inner core with the slurry by means well known in the art. Slurries of inorganic oxides can be prepared by means well known in the art which usually involve the use of a peptizing agent. For example, any of the transitional aluminas can be mixed with water and an acid such as nitric, hydrochloric, or sulfuric to give a slurry. Alternatively, an aluminum sol can be made by for example, dissolving aluminum metal in hydrochloric acid and then mixing the aluminum sol with the alumina powder.

It is also required that the slurry contain an organic bonding agent which aids in the adhesion of the layer material to the inner core. Examples of this organic bonding agent include but are not limited to polyvinyl alcohol (PVA), hydroxy propyl cellulose, methyl cellulose and carboxy methyl cellulose. The amount of organic bonding agent which is added to the slurry will vary considerably from 0.1 wt. % to 3 wt. % of the slurry. How strongly the outer layer is bonded to the inner core can be measured by the amount of layer material lost during an attrition test, i.e., attrition loss. Loss of the second refractory oxide by attrition is measured by agitating the catalyst, collecting the fines and calculating an attrition loss. It has been found that by using an organic bonding agent as described above, the attrition loss is less than 10 wt. % of the outer layer. Finally, the thickness of the outer layer varies from 40 to 400 microns, preferably from 40 microns to 300 microns and more preferably from 45 microns to 200 microns.

Depending on the particle size of the outer refractory inorganic oxide, it may be necessary to mill the slurry in order to reduce the particle size and simultaneously give a narrower particle size distribution. This can be done by means known in the art such as ball milling for times of 30 minutes to 5 hours and preferably from 1.5 to 3 hours. It has been found that using a slurry with a narrow particle size distribution improves the bonding of the outer layer to the inner core.

Without wishing to be bound by any particular theory, it appears that bonding agents such as PVA aid in making an interlocking bond between the outer layer material and the inner core. Whether this occurs by the PVA reducing the surface tension of the core or by some other mechanism is not clear. What is clear is that a considerable reduction in loss of the outer layer by attrition is observed (See examples 8 and 9).

The slurry may also contain an inorganic bonding agent selected from an alumina bonding agent, a silica bonding agent or mixtures thereof. Examples of silica bonding agents include silica sol and silica gel, while examples of alumina bonding agents include alumina sol, boehmite and aluminum nitrate. The inorganic bonding agents are converted to alumina or silica in the finished composition. The amount of inorganic bonding agent varies from 2 to 15 wt. % as the oxide, and based on the weight of the slurry. The use of an inorganic binder is preferred when the outer refractory oxide is a zeolite.

Coating of the inner core with the slurry can be accomplished by means such as rolling, dipping, spraying, etc. One preferred technique involves using a fixed fluidized bed of inner core particles and spraying the slurry into the bed to coat the particles evenly. The thickness of the layer can vary considerably, but usually is from 40 to 400 microns preferably from 40 to 300 microns and most preferably from 50 microns to 200 microns. It should be pointed out that the optimum layer thickness depends on the use for the catalyst and the choice of the outer refractory oxide. Once the inner core is coated with the layer of outer refractory inorganic oxide, the resultant layered composition is dried at a temperature of 100°C to 320°C for a time of 1 to 24 hours and then calcined at a temperature of 400° to 900°C for a time of 0.5 to 10 hours to effectively bond the outer layer to the inner core and provide a layered calcined composition. Of course, the drying and calcining steps can be combined into one step.

When the inner core is composed of a refractory inorganic oxide (inner refractory oxide), it is necessary that the outer refractory inorganic oxide be

different from the inner refractory oxide. Additionally, it is required that the inner refractory inorganic oxide have a substantially lower adsorptive capacity for catalytic metal precursors relative to the outer refractory inorganic oxide.

When the outer refractory inorganic oxide is a zeolite (with or without an inorganic binder) the layered composition can be used to catalyze the alkylation of aromatic hydrocarbons, as will be further detailed below. However, for other processes catalytic metals need to be dispersed onto the layered composition. Catalytic metals can be dispersed on the layered support by means known in the art. Thus, a platinum group metal, a promoter metal and a modifier metal can be dispersed on the outer layer. The platinum group metals include platinum, palladium, rhodium, iridium, ruthenium and osmium. Promoter metals are selected from the group consisting of tin, germanium, rhenium, gallium, bismuth, lead, indium, cerium, zinc and mixtures thereof, while modifier metals are selected from the group consisting of alkali metals, alkaline earth metals and mixtures thereof.

These catalytic metal components can be deposited on the layered support in any suitable manner known in the art. One method involves impregnating the layered support with a solution (preferably aqueous) of a decomposable compound of the metal or metals. By decomposable is meant that upon heating the metal compound is converted to the metal or metal oxide with the release of byproducts. Illustrative of the decomposable compounds of the platinum group metals are chloroplatinic acid, ammonium chloroplatinate, bromoplatinic acid, dinitrodiamino platinum, sodium tetranitroplatinate, rhodium trichloride, hexa-amminerhodium chloride, rhodium carbonylchloride, sodium hexanitrorhodate, chloropalladic acid, palladium chloride, palladium nitrate, diamminepalladium hydroxide, tetraamminepalladium chloride, hexachloroiridate (IV) acid, hexachloroiridate (III) acid, ammonium hexachloroiridate (III), ammonium aquohexachloroiridate (IV), ruthenium tetrachloride, hexachlororuthenate, hexa-ammineruthenium chloride, osmium trichloride and ammonium osmium chloride. Illustrative of the decomposable promoter metal

compounds are the halide salts of the promoter metals. A preferred promoter is tin and preferred decomposable compounds are stannous chloride or stannic chloride.

The alkali and alkaline earth metals which can be used as modifier metals in the practice of this invention include lithium, sodium, potassium, cesium, rubidium, beryllium, magnesium, calcium, strontium and barium. Preferred modifier metals are lithium, potassium, sodium and cesium with lithium and sodium being especially preferred. Illustrative of the decomposable compounds of the alkali and alkaline earth metals are the halide, nitrate, carbonate or hydroxide compounds, e.g., potassium hydroxide, lithium nitrate.

All three types of metals can be impregnated using one common solution or they can be sequentially impregnated in any order, but not necessarily with equivalent results. A preferred impregnation procedure involves the use of a steam-jacketed rotary dryer. The support composition is immersed in the impregnating solution containing the desired metal compound contained in the dryer and the support is tumbled therein by the rotating motion of the dryer. Evaporation of the solution in contact with the tumbling support is expedited by applying steam to the dryer jacket. The resultant composite is allowed to dry under ambient temperature conditions, or dried at a temperature of 80° to 110°C, followed by calcination at a temperature of 200°C to 700°C for a time of 1 to 4 hours, thereby converting the metal compound to the metal or metal oxide. It should be pointed out that for the platinum group metal compound, it is preferred to carry out the calcination at a temperature of 400°C to 700°C.

In one method of preparation, the promoter metal is first deposited onto the layered support composition and calcined as described above and then the modifier metal and platinum group metal are simultaneously dispersed onto the layered support composition by using an aqueous solution which contains a compound of the modifier metal and a compound of the platinum group metal.

The composition is impregnated with the solution as described above and then calcined at a temperature of 400°C to 700°C for a time of 1 to 4 hours.

An alternative method of preparation involves adding one or more of the metal components to the outer refractory oxide prior to applying it as a layer onto the inner core. For example, a decomposable salt of the promoter metal, e.g., tin (IV) chloride can be added to a slurry composed of gamma alumina and aluminum sol. Further, either the modifier metal or the platinum group metal or both can be added to the slurry. Thus, in one method, all three catalytic metals are deposited onto the outer refractory oxide prior to depositing the second refractory oxide as a layer onto the inner core. Again, the three types of catalytic metals can be deposited onto the outer refractory oxide powder in any order although not necessarily with equivalent results.

One preferred method of preparation involves first impregnating the promoter metal onto the outer refractory oxide and calcining as described above. Next, a slurry is prepared (as described above) using the outer refractory oxide containing the promoter metal and applied to the inner core by means described above. Finally, the modifier metal and platinum group metal are simultaneously impregnated onto the layered composition which contains the promoter metal and calcined as described above to give the desired layered catalyst. This method of preparation is preferred when the catalyst is used in a dehydrogenation process. Other methods, as described above, may be preferred when the catalyst is to be used for other processes.

As a final step in the preparation of the layered catalyst composition, the catalyst composition is reduced under hydrogen or other reducing atmosphere in order to ensure that the platinum group metal component is in the metallic state (zero valent). Reduction is carried out at a temperature of 100°C to 650°C for a time of 0.5 to 10 hours in a reducing environment, preferably dry hydrogen. The state of the promoter and modifier metals can be metallic (zero valent), metal oxide or metal oxychloride.

The layered catalyst composition can also contain a halogen component which can be fluorine, chlorine, bromine, iodine or mixtures thereof with chlorine and bromine preferred. This halogen component is present in an amount of 0.03 to 1.5 wt. % with respect to the weight of the entire catalyst composition. The halogen component can be applied by means well known in the art and can be done at any point during the preparation of the catalyst composition although not necessarily with equivalent results. It is preferred to add the halogen component after all the catalytic components have been added either before or after treatment with hydrogen.

Although in the preferred embodiments all three metals are uniformly distributed throughout the outer layer of the outer refractory oxide and substantially present only in the outer layer, it is also within the bounds of this invention that the modifier metal can be present both in the outer layer and the inner core. This is owing to the fact that the modifier metal can migrate to the inner core, when the core is other than a metallic core.

Although the concentration of each metal component can vary substantially, it is desirable that the platinum group metal be present in a concentration of 0.01 to 5 weight percent on an elemental basis of the entire weight of the catalyst and preferably from 0.05 to 2.0 wt.%. The promoter metal is present in an amount from 0.05 to 10 wt.% of the entire catalyst while the modifier metal is present in an amount from 0.1 to 5 wt.% and preferably from 2 to 4 wt.% of the entire catalyst. Finally, the atomic ratio of the platinum group metal to modifier metal varies from 0.05 to 5. In particular when the modifier metal is tin, the atomic ratio is from 0.1:1 to 5:1 and preferably from 0.5:1 to 3:1. When the modifier metal is germanium the ratio is from 0.25:1 to 5:1 and when the promoter metal is rhenium, the ratio is from 0.05:1 to 2.75:1.

The various layered compositions described above can be used in a variety of hydrocarbon conversion process. For example, a layered composition in which the outer layer comprises a zeolite and an inorganic binder has

particular use for the alkylation of aromatic hydrocarbons by olefins. The alkylation and preferably the monoalkylation of aromatic compounds involves reacting an aromatic compound with an olefin using the above described layered composition. The olefins which can be used in the instant process are any of those which contain from 2 up to 20 carbon atoms. These olefins may be branched or linear olefins and either terminal or internal olefins. Preferred olefins are ethylene, propylene and those olefins which are known as detergent range olefins. Detergent range olefins are linear olefins containing from 6 up through 20 carbon atoms which have either internal or terminal double bonds. Linear olefins containing from 8 to 16 carbon atoms are preferred and those containing from 10 up to 14 carbon atoms are especially preferred.

The alkylatable aromatic compounds may be selected from the group consisting of benzene, naphthalene, anthracene, phenanthrene, and substituted derivatives thereof, with benzene and its derivatives being the most preferred aromatic compound. By alkylatable is meant that the aromatic compound can be alkylated by an olefinic compound. The alkylatable aromatic compounds may have one or more of the substituents selected from the group consisting of alkyl groups (having from 1 to 20 carbon atoms), hydroxyl groups, and alkoxy groups whose alkyl group also contains from 1 up to 20 carbon atoms. Where the substituent is an alkyl or alkoxy group, a phenyl group can also be substituted on the alkyl chain. Although unsubstituted and monosubstituted benzenes, naphthalenes, anthracenes, and phenanthrenes are most often used in the practice of this invention, polysubstituted aromatics also may be employed. Examples of suitable alkylatable aromatic compounds in addition to those cited above include biphenyl, toluene, xylene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene, hexylbenzene, heptylbenzene, octylbenzene, etc.; phenol, cresol, anisole, ethoxy-, propoxy-, butoxy-, pentoxy-, hexoxybenzene, etc.

The particular conditions under which the monoalkylation reaction is conducted depends upon the aromatic compound and the olefin used. One necessary condition is that the reaction be conducted under at least partial liquid phase conditions. Therefore, the reaction pressure is adjusted to maintain the

olefin at least partially dissolved in the liquid phase. For higher olefins the reaction may be conducted at autogenous pressure. As a practical matter the pressure normally is in the range between 200 and 1,000 psig (1379-6985 kPa) but usually is in a range between 300-600 psig (2069-4137 kPa). The alkylation of the alkylatable aromatic compounds with the olefins in the C₂-C₂₀ range can be carried out at a temperature of 60°C to 400°C, and preferably from 90°C to 250°C, for a time sufficient to form the desired product. In a continuous process this time can vary considerably, but is usually from 0.1 to 3 hr⁻¹ weight hourly space velocity with respect to the olefin. In particular, the alkylation of benzene with ethylene can be carried out at temperatures of 200°C to 250°C and the alkylation of benzene by propylene to give cumene at a temperature of 90°C to 200°C. The ratio of alkylatable aromatic compound to olefin used in the instant process will depend upon the degree of selective monoalkylation desired as well as the relative costs of the aromatic and olefinic components of the reaction mixture. For alkylation of benzene by propylene, benzene-to-olefin ratios may be as low as 1 and as high as 10, with a ratio of 2.5-8 being preferred. Where benzene is alkylated with ethylene a benzene-to-olefin ratio between 1:1 and 8:1 is preferred. For detergent range olefins of C₆-C₂₀, a benzene-to-olefin ratio of between 5:1 up to as high as 30:1 is generally sufficient to ensure the desired monoalkylation selectivity, with a range between 8:1 and 20:1 even more preferred.

The zeolites of this invention can also be used to catalyze transalkylation which is included in the general term "alkylation". By "transalkylation" is meant that process where an alkyl group on one aromatic nucleus is intermolecularly transferred to a second aromatic nucleus. A preferred transalkylation process is one where one or more alkyl groups of a polyalkylated aromatic compound is transferred to a nonalkylated aromatic compound, and is exemplified by reaction of diisopropylbenzene with benzene to give two molecules of cumene. Thus, transalkylation often is utilized to add to the selectivity of a desired selective monoalkylation by reacting the polyalkylates invariably formed during alkylation with nonalkylated aromatic to form additional monoalkylated products. For the purposes of this process, the polyalkylated aromatic compounds are those formed

in the alkylation of alkylatable aromatic compounds with olefins as described above, and the nonalkylated aromatic compounds are benzene, naphthalene, anthracene, and phenanthrene. The reaction conditions for transalkylation are similar to those for alkylation, with temperatures being in the range of 100 to 250°, pressures in the range of 100 to 750 psig, and the molar ratio of unalkylated aromatic to polyalkylated aromatic in the range from 1 to 10. Examples of polyalkylated aromatics which may be reacted with, e.g., benzene as the nonalkylated aromatic include diethylbenzene, diisopropylbenzene, dibutylbenzene, triethylbenzene, triisopropylbenzene etc.

When the layered compositions of this invention contain catalytic metals and optionally promoters and modifiers, they can be used in hydrocarbon conversion processes such as alkylation of isoparaffins, hydrocracking, cracking isomerization, hydrogenation, dehydrogenation and oxidation. The conditions for carrying out these processes are well known in the art and are presented here for completeness.

Hydrocracking conditions typically include a temperature in the range of 240°C to 649°C (400°F-1200°F), preferably between 316°C and 510°C (600-950°F). Reaction pressures are in the range of atmospheric to 24,132 kPag (3,500 psig), preferably between 1,379 and 20,685 kPag (200 - 3,000 psig). Contact times usually correspond to liquid hourly space velocities (LHSV) in the range of 0.1 hr⁻¹ to 15 hr⁻¹, preferably between 0.2 and 3 hr⁻¹. Hydrogen circulation rates are in the range of 178 to 8,888 standard cubic meters per cubic meter of charge (1,000 to 50,000 standard cubic feet (scf) per barrel of charge) preferably between 355 to 5,333 std. m³/m³ (2,000 and 30,000 scf per barrel of charge).

The reaction zone effluent is normally removed from the catalyst bed, subjected to partial condensation and vapor-liquid separation and then fractionated to recover the various components thereof. The hydrogen, and if desired some or all of the unconverted heavier materials, are recycled to the reactor. Alternatively, a two-stage flow may be employed with the unconverted

material being passed into a second reactor. Catalysts of the subject invention may be used in just one stage of such a process or may be used in both reactor stages.

Catalytic cracking processes are preferably carried out with the catalyst composition using feedstocks such as gas oils, heavy naphthas, deasphalted crude oil residua, etc. with gasoline being the principal desired product. Temperature conditions of 454°C to 593°C (850° to 1100°F,) LHSV values of 0.5 to 10 hr⁻¹ and pressure conditions of from 0 to 345 kPag (50 psig) are suitable.

Isomerization reactions are carried out in a temperature range of 371°C to 538°C (700 – 1000°F). Olefins are preferably isomerized at temperatures of 260°C to 482°C (500°F to 900°F), while paraffins, naphthenes and alkyl aromatics are isomerized at temperatures of 371°C to 538°C (700°F to 1000°F). Hydrogen pressures are in the range of 689 to 3,445 kPag (100 to 500 psig). Contact times usually correspond to liquid hourly space velocities (LHSV) in the range of 0.1 hr⁻¹ to 10 hr⁻¹. Hydrogen to hydrocarbon molar ratios are in the range of 1 to 20, preferably between 4 and 12.

In a dehydrogenation process, dehydrogenatable hydrocarbons are contacted with the catalyst of the instant invention in a dehydrogenation zone maintained at dehydrogenation conditions. This contacting can be accomplished in a fixed catalyst bed system, a moving catalyst bed system, a fluidized bed system, etc., or in a batch-type operation. A fixed bed system is preferred. In this fixed bed system the hydrocarbon feed stream is preheated to the desired reaction temperature and then flowed into the dehydrogenation zone containing a fixed bed of the catalyst. The dehydrogenation zone may itself comprise one or more separate reaction zones with heating means there between to ensure that the desired reaction temperature can be maintained at the entrance to each reaction zone. The hydrocarbon may be contacted with the catalyst bed in either upward, downward or radial flow fashion. Radial flow

of the hydrocarbon through the catalyst bed is preferred. The hydrocarbon may be in the liquid phase, a mixed vapor-liquid phase or the vapor phase when it contacts the catalyst. Preferably, it is in the vapor phase.

Hydrocarbons which can be dehydrogenated include hydrocarbons with 2 to 30 or more carbon atoms including paraffins, isoparaffins, alkylaromatics, naphthenes and olefins. A preferred group of hydrocarbons is the group of normal paraffins with 2 to 30 carbon atoms. Especially preferred normal paraffins are those having 2 to 15 carbon atoms.

Dehydrogenation conditions include a temperature of from 400°C to 900°C, a pressure of from 1 to 1013 kPa and a liquid hourly space velocity (LHSV) of from 0.1 to 100 hr⁻¹. Generally for normal paraffins the lower the molecular weight the higher the temperature required for comparable conversion. The pressure in the dehydrogenation zone is maintained as low as practicable, consistent with equipment limitations, to maximize the chemical equilibrium advantages.

The effluent stream from the dehydrogenation zone generally will contain unconverted dehydrogenatable hydrocarbons, hydrogen and the products of dehydrogenation reactions. This effluent stream is typically cooled and passed to a hydrogen separation zone to separate a hydrogen-rich vapor phase from a hydrocarbon-rich liquid phase. Generally, the hydrocarbon-rich liquid phase is further separated by means of either a suitable selective adsorbent, a selective solvent, a selective reaction or reactions or by means of a suitable fractionation scheme. Unconverted dehydrogenatable hydrocarbons are recovered and may be recycled to the dehydrogenation zone. Products of the dehydrogenation reactions are recovered as final products or as intermediate products in the preparation of other compounds.

The dehydrogenatable hydrocarbons may be admixed with a diluent material before, while or after being flowed to the dehydrogenation zone. The diluent material may be hydrogen, steam, methane, ethane, carbon dioxide,

nitrogen, argon and the like or a mixture thereof. Hydrogen is the preferred diluent. Ordinarily, when hydrogen is utilized as the diluent it is utilized in amounts sufficient to ensure a hydrogen to hydrocarbon mole ratio of 0.1:1 to 40:1, with best results being obtained when the mole ratio range is 1:1 to 10:1. The diluent hydrogen stream passed to the dehydrogenation zone will typically be recycled hydrogen separated from the effluent from the dehydrogenation zone in the hydrogen separation zone.

Water or a material which decomposes at dehydrogenation conditions to form water such as an alcohol, aldehyde, ether or ketone, for example, may be added to the dehydrogenation zone, either continuously or intermittently, in an amount to provide, calculated on the basis of equivalent water, 1 to 20,000 weight ppm of the hydrocarbon feed stream. Adding 1 to 10,000 weight ppm of water gives best results when dehydrogenating paraffins having from 2 to 30 or more carbon atoms.

Hydrogenation processes can be carried out using reactors and hydrogenation zones similar to the dehydrogenation process described above. Specifically, hydrogenation conditions include pressures of 0 kPag to 13,789 kPag, temperatures of 30°C to 280°C, H₂ to hydrogenatable hydrocarbon mole ratios of 5:1 to 0.1:1 and LHSV of 0.1 to 20 hr⁻¹.

The layered compositions of this invention can also be used in oxidation reactions. These oxidation reactions include:

- 1) partial oxidation of hydrocarbon streams, such as naphtha or methane, to generate synthesis gas (CO + H₂);
- 2) selective oxidation of hydrogen produced from endothermic dehydrogenation reactions such as ethylbenzene to styrene; and,
- 3) oxidation of methane, ethane or carbon monoxide to clean up flue gas emissions from combustion processes.

The layered sphere catalyst will be of most benefit to processes where the activity or selectivity of the catalyst is limited by intraparticle diffusional resistance of product or reactants.

The conditions for the oxidation process depend on the individual process application but are generally 350°C to 800°C, 40 kPa to 2030 kPa, with a diluent present in the feedstream such as N₂, CO₂, H₂O to control the reaction. Hydrogen may also be present as a diluent and also a reactant. For the selective oxidation of hydrogen, the molar ratio of oxygen to H₂ may vary from 0.05 to 0.5. The diluent level is generally from 0.1 to 10 moles of diluent per mole of hydrocarbon. For example, the steam to ethylbenzene molar ratio may be from 5:1 to 7:1 during the dehydrogenation of ethylbenzene. Typical space velocity for oxidation is between 0.5 to 50 hr⁻¹ LHSV.

The following examples are presented in illustration of this invention and are not intended as undue limitations on the generally broad scope of the invention as set out in the appended claims.

EXAMPLE 1

Alumina spheres were prepared by the well known oil drop method which is described in U. S.-A- 2, 620,314. This process involves forming an aluminum hydrosol by dissolving aluminum in hydrochloric acid. Hexamethylene tetraamine was added to the sol to gel the sol into spheres when dispersed as droplets into an oil bath maintained at 93°C. The droplets remained in the oil bath until they set and formed hydrogel spheres. After the spheres were removed from the hot oil, they were pressure aged at 135°C and washed with dilute ammonium hydroxide solution, dried at 110°C and calcined at 650°C for about 2 hours to give gamma alumina spheres. The calcined alumina was now crushed into a fine powder having a particle size of less than 200 microns.

Next, a slurry was prepared by mixing 258 g of an aluminum sol (20 wt. % Al_2O_3) and 6.5 g of a 50% aqueous solution of tin chloride and 464 g of deionized water and agitated to uniformly distribute the tin component. To this mixture there were added 272 g of the above prepared alumina powder, and the slurry was ball milled for 2 hours thereby reducing the maximum particle size to less than 40 microns. This slurry (1,000 g) was sprayed onto 1 kg of alpha alumina cores having an average diameter of 1.05 mm by using a granulating and coating apparatus for 17 minutes to give an outer layer of 74 microns. At the end of the process, 463 g of slurry were left which did not coat the cores. This layered spherical support was dried at 150°C for 2 hours and then calcined at 615°C for 4 hours in order to convert the pseudoboehmite in the outer layer into gamma alumina and convert the tin chloride to tin oxide.

The calcined layered support (1150 g) was impregnated with lithium using a rotary impregnator by contacting the support with an aqueous solution (1:1 solution: support volume ratio) containing lithium nitrate and 2 wt.% nitric acid based on support weight. The impregnated catalyst was heated using the rotary impregnator until no solution remained, dried, and then calcined at 540°C for 2 hours.

The tin and lithium containing composite was now impregnated with platinum by contacting the above composite with an aqueous solution (1:1 solution: support volume ratio) containing chloroplatinic acid and 1.2 wt.% hydrochloric acid (based on support weight). The impregnated composite was heated using the rotary impregnator until no solution remained, dried and calcined at 540°C for 2½ hours and reduced in hydrogen at 500°C for 2 hours. Elemental analysis showed that this catalyst contained 0.093 wt.% platinum, 0.063 wt.% tin and 0.23 wt.% lithium with respect to the entire catalyst. This catalyst was identified as catalyst A. The distribution of the platinum was determined by Electron Probe Micro Analysis (EPMA) using a Scanning Electron Microscope which showed that the platinum was evenly distributed throughout the outer layer only.

EXAMPLE 2

The procedure of Example 1 was repeated, except that a slurry was prepared by mixing 275 g of an alumina sol into 431 g of deionized water with sufficient agitation, and then adding 289 g of gamma alumina powder, 5.36 g of a 50% aqueous solution of tin chloride was used, and after granulation and coating, the layered spherical support had an outer layer of 99 microns in thickness. There were 248 g of slurry left after the coating was carried out. Elemental analysis (wt.% based on the entire catalyst) showed that this catalyst contained 0.09 wt.% platinum, 0.09 wt.% tin and 0.23 wt.% lithium and was identified as catalyst B. Catalyst B was analyzed by EPMA which showed that the platinum was evenly distributed throughout the outer layer only.

COMPARATIVE EXAMPLE 1

A catalyst was prepared in a similar way to that of example II of U.S.-A- 4,786,625 except that the solution was sprayed onto the support. The catalyst was analyzed and found to contain 0.43 wt.% platinum, 1.7 wt.% tin and 0.62 wt.% lithium. This catalyst was identified as catalyst C. Catalyst C was analyzed by EPMA which showed that the platinum was on the surface of the support.

COMPARATIVE EXAMPLE 2

A catalyst was prepared according to example I of U.S.-A- 4,786,625. This catalyst was analyzed and found to contain 0.43 wt.% platinum, 0.48 wt.% tin and 0.58 wt. % lithium. This catalyst was identified as catalyst D. All the metals were evenly distributed throughout the support.

EXAMPLE 3

A gamma alumina slurry (1000g) was prepared as in example 1 except that no tin chloride was added to the slurry. This slurry was applied to 1000g of alpha alumina cores having a diameter of 1.054mm as in example 1 and

calcined as in example 1 to give a layered support with an outer gamma-alumina layer of 74 microns in thickness.

The layered support (202g) was contacted with an aqueous solution prepared by diluting a 50% tin chloride solution (Sn content: 0.144g based on metal) and nitric acid (HNO₃ content: 18.2g) with deionized water to a volume of 150 ml. The mixture was dried in a rotary evaporator at a temperature of 150°C for 2 hours, following by calcination at a temperature of 615°C for 4 hours.

The tin containing layered composition of the previous paragraph was now impregnated with lithium and platinum using a rotary impregnator by contacting the composition with an aqueous solution containing chloroplatinic acid (Pt = 0.188g), lithium nitrate (Li = 0.54g) and nitric acid. The impregnated catalyst composition was heated in the rotary evaporator until no solution remained, calcined at 540°C for 2 ½ hours and then reduced in hydrogen at 500°C for 2 hours. The platinum and tin were determined by EPMA to be evenly distributed throughout the outer layer. Elemental analysis showed that this layered catalyst composition contained 0.093 wt.% platinum, 0.071 wt.% tin and 0.268 wt. % lithium calculated as the metal and based on the entire catalyst weight. This catalyst was identified as catalyst E.

EXAMPLE 4

A sample of 600 ml. of spherical alumina was prepared as in example 1. This alumina was impregnated using a rotary impregnator with an aqueous solution prepared by diluting 9.55 g of a 50% tin chloride solution and 49.6 g of a 61% nitric acid solution with deionized water to a volume of 420 ml. The impregnated alumina spheres were dried in the rotary evaporator and then calcined at 540°C for 2 ½ hours.

The resulting tin-containing catalyst was impregnated with an aqueous solution containing platinum and lithium, prepared by diluting a chloroplatinic acid solution (Pt content: 1.71 g), a lithium nitrate solution (Li content: 1.16 g)

and 6.61 g of a 61% nitric acid solution with deionized water to a volume of 420 ml. The obtained spherical catalyst was dried in a rotary evaporator until no solution remained and then calcined at a temperature of 540°C for 2.5 hours. The platinum and tin were evenly distributed throughout the sphere.

A slurry was prepared by mixing 600 ml of the above spherical catalyst with 4.0 g of P-salt (dinitrodiammineplatinum in nitric acid) 0.641 g of meta stannic acid and 202 g of alumina sol (20 wt.% Al_2O_3) with 1204 g of deionized water and ball milling the mixture for 4 hours. This slurry was now used to apply a layer onto an alpha-alumina core having a diameter of 1.054 mm as in example 1. A layered catalyst was obtained which had a layer of 50 microns. This layered catalyst composition was dried at 150°C for 2 hrs. and then calcined at 615°C for 4 hours to convert the pseudoboehmite in the outer layer to gamma alumina. Finally, the catalyst composition was reduced in hydrogen at 500°C for 2 hours. Elemental analysis showed that this catalyst contained 0.089 wt.% platinum, 0.113 wt. % tin and 0.05 wt.% lithium, all calculated on an elemental basis and based on the weight of the entire catalyst. This catalyst was identified as catalyst F.

EXAMPLE 5

The catalysts of examples 1-4 and comparative examples 1 and 2 were tested for dehydrogenation activity. In a 1.27 cm (1/2") reactor, 10 cc of catalyst was placed and a hydrocarbon feed composed of 8.8 wt. % n-C₁₀, 40.0 wt. % n-C₁₁, 38.6 wt. % n-C₁₂, 10.8 wt. % n-C₁₃, 0.8 wt. % n-C₁₄ and 1 vol. % non-normals was flowed over the catalyst under a pressure of 138 kPa (20 psig), a H₂: hydrocarbon molar ratio of 6:1 and a liquid hourly space velocity (LHSV) of 20 hr⁻¹. Water at a concentration of 2000 ppm based on hydrocarbon weight was injected. The total normal olefin concentration in the product (% TNO) was maintained at 15 wt. % by adjusting reactor temperature.

The results of the testing are presented in Table 1. What is presented is the deactivation rate (slope) which is obtained by plotting temperature (°F)

needed to maintain 15% TNO versus time. Selectivity for TNO at 120 hours on stream is also presented and is calculated by dividing % TNO by total conversion. Finally, non-TNO selectivity is 100% - %TNO.

Table 1

Comparison of Layered versus Non-Layered Catalysts

Catalyst I.D.	Deactivation Rate(°F/hr)	TNO Selectivity (wt.%)	Non-TNO Selectivity (wt.%)
A	0.052	94.6	5.4
B	0.032	94.0	6.0
C	0.067	93.5	6.5
D	0.05	91.1	8.9
E	0.050	94.4	5.6
F	0.033	94.0	6.0

The results show that the layered catalysts of the invention have both lower deactivation rates and increased selectivity to normal olefins versus catalysts of the prior art. Specifically, comparing catalysts A, B, E and F with catalyst C (platinum on the surface), it is observed that the deactivation rate is smaller for catalysts A, B, E and F. Additionally, selectivity is better for the layered catalysts of the invention. It must be pointed out that when selectivities are this high, one must look at the residual amount left or the non-TNO selectivity. Here, the amount of non-TNO for catalysts A and E are 17 wt.% and 14 wt. % less, respectively, than for catalyst C which is a substantial improvement.

Comparing catalysts A, B, E and F with catalyst D (uniform platinum) what is observed is that catalysts B and F have a much lower deactivation rate

than catalyst D, while catalysts A and E have a much higher selectivity (39 and 37 wt.% less non-TNO make, respectively) than catalyst D. Again, this shows a marked improvement in stability and selectivity.

EXAMPLE 6

The procedure set forth in example 1 was used to prepare a catalyst with the modification that polyvinyl alcohol (PVA) at a concentration of 2 wt. % of the gamma alumina was added to the slurry. This catalyst was identified as catalyst G.

EXAMPLE 7

The procedure set forth in example 1 was used to prepare a catalyst with the modification that hydroxy propyl cellulose (HPC) at a concentration of 2 wt. % of the gamma alumina was added to the slurry. This catalyst was identified as catalyst H.

EXAMPLE 8

The procedure in example 1 was used to prepare a catalyst with a layer thickness of 90 microns. This catalyst was identified as catalyst I.

EXAMPLE 9

Catalysts G, H and I were tested for loss of layer material by attrition using the following test.

A sample of the catalyst was placed in a vial which in turn was placed in a blender mill along with two other vials containing the same amount of catalyst sample. The vials were milled for ten (10) minutes, the vials removed and then sieved to separate the powder from the spheres. The powder was weighed and an attrition loss (wt.%) was calculated.

The results of the attrition test are summarized in Table 2.

Table 2**Effect of Organic Binding Agent on Attrition**

<u>Catalyst I.D.</u>	<u>Weight Percent Loss</u>	
	<u>Based on Total Amount</u>	<u>Based On Layer</u>
G (PVA)	1.0	4.3
H (HPC)	1.9	8.5
I (No Additive)	3.7	17.9

The data in Table 2 show that using an organic binding agent greatly improves the attrition loss of a layered catalyst.

WHAT IS CLAIMED IS:

1. A layered catalyst composition comprising an inner core, an outer layer bonded to said inner core, the outer layer bonded to the inner core to the extent that the attrition loss is less than 10 wt.% based on the weight of the outer layer and, the outer layer comprising an outer refractory inorganic oxide optionally having uniformly dispersed thereon at least one platinum group metal, a promoter metal and a modifier metal, an organic binder, and when the inner core is an inorganic oxide the outer refractory inorganic oxide is different from the inner core inorganic oxide.
2. The composition of claim 1, where the inner core is selected from the group consisting of alpha alumina, theta alumina, silicon carbide, metals, cordierite, zirconia, titania and mixtures thereof.
3. The composition of claim 1, where the outer refractory inorganic oxide is selected from the group consisting of gamma alumina, delta alumina, eta alumina, theta alumina, silica/alumina, zeolites, nonzeolitic molecular sieves, titania, zirconia and mixtures thereof.
4. The composition of claims 1, 2 or 3, where the outer layer comprises a zeolite.
5. A process for preparing the layered composition described in any one of claims 1 to 4 comprising:
 - (a) coating the inner core with a slurry comprising the outer refractory inorganic oxide and an organic bonding agent, the outer refractory inorganic oxide having dispersed thereon at least one promoter metal, drying the coated core and calcining at a temperature of 400°C to 900°C for a time sufficient to bond the outer layer to the inner core and provide a layered support;
 - (b) uniformly dispersing on the layered support of step (a) the modifier metal and a platinum metal to give a product and
 - (c) reducing the product of step (b) at reduction conditions to provide the layered catalyst composition.

6. A hydrocarbon conversion process comprising contacting a hydrocarbon stream with the layered composition described in any one of claims 1 to 4 under hydrocarbon conversion conditions to give a converted product.
7. The process of claim 6, where the hydrocarbon conversion process is selected from the group consisting of hydrogenation, dehydrogenation, oxidation and aromatic alkylation.
8. The process of claim 7, where the process is dehydrogenation and the dehydrogenatable hydrocarbon is a paraffin having 2 to 30 carbon atoms.
9. The process of claim 7, where the process is the alkylation of aromatic hydrocarbons with olefins.
10. The process of claim 9, where the aromatic hydrocarbon is selected from benzene, naphthalene, anthracene and phenanthrene and the olefin contain from 2 to 20 carbon atoms.