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(54) Title: ACIDIC SOLID OXIDES

(57) Abstract

There is provided an acidic solid comprising a Group IVB metal oxide modified with an oxyanion of a Group VIB metal. An example of this acidic solid is zirconia, modified with tungstate. This acidic solid also comprises an oxide of Mn or Fe. This acidic solid may be used as a catalyst, for example, to isomerize C_4 to C_8 paraffins. The acidic solid may be prepared by co-precipitating the Group IVB metal oxide along with the oxyanion of the Group VIB metal.

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ACIDIC SOLID OXIDES

There is provided an acidic solid comprising a Group IVB metal oxide modified with an oxyanion of a Group VIB metal. The acidic solid further comprises an oxide of Mn and/or Fe. This modified solid oxide may be used as a catalyst, for example, to isomerize C_4 to C_8 paraffins. The modified solid oxide may be prepared by co-precipitating the Group IVB metal oxide along with the oxyanion of the Group VIB metal.

The present catalysts, especially tungstate-modified zirconia catalysts, are useful for many hydrocarbon conversion processes such as paraffin isomerization, ring opening of cyclics, alkylation of naphthalene, hydrocracking, etc. These catalysts may be prepared by a complex impregnation procedure involving numerous steps including the precipitation of zirconia precursor, refluxing, two filtration/washing/reslurry steps, impregnation with tungsten, and a final calcination. In a more preferred method, this complex procedure is reduced to just three steps: co-precipitation of tungsten with the zirconia precursor, filtration, and calcination.

The co-precipitation method produces a better catalyst at lower manufacturing cost (fewer steps) and is more flexible to address potential environmental concerns.

The solid material described herein comprises an oxide of a Group IVB metal, such as zirconia or titania. This Group IVB metal oxide is modified with an oxyanion of a Group VIB metal, such as an oxyanion of tungsten, such as tungstate. The modification of the Group IVB metal oxide with the oxyanion of the Group VIB metal imparts acid functionality to the material. The modification of a Group IVB metal oxide, particularly, zirconia, with a Group VIB metal oxyanion, particularly tungstate, is described in U.S. Patent No. 5,113,034; in Japanese Kokai Patent Application No. Hei 1 [1989]-288339; and in an article by K. Arata and M. Hino in <u>Proceedings 9th International</u>

<u>Congress on Catalysis</u>, Volume 4, pages 1727-1735 (1988). According to these publications, tungstate is impregnated onto a preformed solid zirconia material.

For the purposes of the present disclosure, the expression, Group IVB metal oxide modified with an oxyanion of a Group VIB metal, is intended to connote a material comprising, by elemental analysis, a Group IVB metal, a Group VIB metal and oxygen, with more acidity than a simple mixture of separately formed Group IVB metal oxide mixed with a separately formed Group VIB metal oxide or oxyanion. The present Group IVB metal, e.g., zirconium, oxide modified with an oxyanion of a Group VIB metal, e.g., tungsten, is believed to result from an actual chemical interaction between a source of a Group IVB metal oxide and a source of a Group VIB metal oxide or oxyanion.

This chemical interaction is discussed in the aforementioned article by K. Arata and M. Hino in <u>Proceedings 9th International Congress on Catalysis</u>, Volume 4, pages 1727-1735 (1988). In this article, it is suggested that solid superacids are formed when sulfates are reacted with hydroxides or oxides of certain metals, e.g., Zr. These superacids are said to have the structure of a bidentate sulfate ion coordinated to the metal, e.g., Zr. In this article, it is further suggested that a superacid can also be formed when tungstates are reacted with hydroxides or oxides of Zr. The resulting tungstate modified zirconia materials are theorized to have an analogous structure to the aforementioned superacids comprising sulfate and zirconium, wherein tungsten atoms replace sulfur atoms in the bidentate structure.

Although it is believed that the present catalysts may comprise the bidentate structure suggested in the aforementioned article by Arata and Hino, the particular structure of the catalytically active site in the present Group IVB metal oxide modified with an oxyanion of a Group VIB metal has not yet been confirmed, and it is not intended that this catalyst component should be limited to any particular structure.

There is provided an acidic solid comprising a Group IVB metal oxide modified with an oxyanion of a Group VIB metal, said acidic solid further comprising an oxide of at least one metal selected from the group consisting of iron and manganese.

There is also provided a method for preparing an acidic solid comprising a Group IVB metal oxide modified with an oxyanion of a Group VIB metal, said method comprising co-precipitating a source of a Group IVB metal oxide, a source of an oxyanion of a Group VIB metal, and a source of an oxide of metal selected from the group consisting of Fe and Mn.

There is also provided a method for preparing an acidic solid comprising tungstate-modified zirconia, said method comprising the steps of:

(a) combining a first liquid solution with a second liquid solution and a third liquid solution, said first solution comprising a source of zirconia dissolved in water, said second solution comprising a source of tungstate dissolved in water, and said third solution comprising a source of at least one oxide selected from the group consisting of iron and manganese;

(b) maintaining the combined solutions of step (a) under conditions sufficient to form a solid co-precipitate comprising tungstate-modified zirconia and at least one compound comprising Fe and/or Mn;

(c) recovering the solid co-precipitate from step (b) by filtration; and

(d) calcining the recovered co-precipitate from step (c).

There is also provided a process for converting an organic compound, said process comprising contacting said organic compound with a catalyst under sufficient conversion conditions, wherein said catalyst comprises an acidic solid comprising a Group IVB metal oxide modified with an oxyanion of a Group VIB metal, said acidic solid further comprising an oxide of at least one metal selected from the group consisting of iron and manganese.

There is also provided a process for isomerizing hydrocarbons, said process comprising contacting a feed comprising C_4 to C_8 hydrocarbons with an isomerization catalyst under sufficient isomerization conditions, said isomerization catalyst comprising (i) a noble metal and (ii) an acidic solid comprising a Group IVB metal oxide modified with an oxyanion of a Group VIB metal, said acidic solid further comprising an oxide of at least one metal selected from the group consisting of iron and manganese.

Suitable sources of the Group IVB metal oxide, used for preparing the present catalyst, include compounds capable of generating such oxides, such as oxychlorides, chlorides, nitrates, oxynitrates, etc., particularly of zirconium or titanium. Alkoxides of such metals may also be used as precursors or sources of the Group IVB metal oxide. Examples of such alkoxides include zirconium n-propoxide and titanium i-propoxide. These sources of a Group IVB metal oxide, particularly zirconia, may form zirconium hydroxide, i.e., $Zr(OH)_4$, or hydrated zirconia as intermediate species upon precipitation from an aqueous medium in the absence of a reactive source of tungstate. The expression, hydrated zirconia, is intended to connote materials comprising zirconium atoms covalently linked to other zirconium atoms via bridging oxygen atoms, i.e., Zr-O-Zr, further comprising available surface hydroxy groups. When hydrated zirconia is impregnated with a suitable source of tungstate under sufficient conditions, these available surface hydroxyl groups are believed to react with the source of tungstate to form an acidic catalyst. As suggested in the aforementioned article by K. Arata and M. Hino in <u>Proceedings 9th International Congress on Catalysis</u>, Volume 4, pages 1727-1735 (1988), precalcination of $Zr(OH)_4$ at a temperature of from about 100°C to about 400°C results in a species which interacts more favorably with tungstate upon impregnation therewith. This precalcination is believed to result in the condensation of ZrOH groups to form a polymeric zirconia species with surface hydroxyl groups. This polymeric species is referred to herein as a form of a hydrated zirconia.

Suitable sources for the oxyanion of the Group VIB metal, particularly molybdenum or tungsten, include, but are not limited to, ammonium metatungstate or metamolybdate, tungsten or molybdenum chloride, tungsten or molybdenum carbonyl, tungstic or molybdic acid and sodium tungstate or molybdate.

The present modified oxide material may be prepared by combining a first liquid solution comprising a source of a Group IVB metal oxide with a second liquid solution comprising a source of an oxyanion of a Group VIB metal. This combination of two solutions takes place under conditions sufficient to cause co-precipitation of the modified oxide material as a solid from the liquid medium. Alternatively, the source of the Group IVB metal oxide and the source of the oxyanion of the Group VIB metal may be combined in a single liquid solution. This solution may then be subjected to conditions sufficient to cause co-precipitation of the solid modified oxide material, such as by the addition of a precipitating reagent to the solution. Water is a preferred solvent for these solutions.

The temperature at which the liquid medium is maintained during the co-precipitation may be less than about 200°C, e.g., from about 0°C to about 200°C. This liquid medium may be maintained at an ambient temperature (i.e., room temperature) or the liquid may be cooled or heated. A particular range of such temperatures is from about 50°C to about 100°C.

The liquid medium from which the present catalyst components are co-precipitated may optionally comprise a solid support material, in which case the present catalyst may be co-precipitated directly onto the solid support material. Examples of such support materials include the material designated M41S, which is described in U.S. Patent No. 5,102,643. A particular example of such an M41S material is a material designated MCM-41, which is described in U.S. Patent No. 5,098,684.

Support materials and/or co-catalyst materials may also, optionally, be co-precipitated from the liquid medium along with the Group IVB metal oxide and the oxyanion of the Group VIB metal. An example of a co-catalyst material is a hydrogenation/dehydrogenation component.

According to an optional modification of the solid material described herein, a hydrogenation/dehydrogenation component is combined with the material. This hydrogenation/dehydrogenation component imparts the ability of the material to catalyze the addition of hydrogen to or the removal of hydrogen from organic compounds, such as hydrocarbons, optionally substituted with one or more heteroatoms, such as oxygen, nitrogen, metals or sulfur, when the organic compounds are contacted with the modified material under sufficient hydrogenation or dehydrogenation conditions.

Examples of hydrogenation/dehydrogenation components include the oxide, hydroxide or free metal (i.e., zero valent) forms of Group VIII metals (i.e., Pt, Pd, Ir, Rh, Os, Ru, Ni, Co and Fe), Group IVA metals (i.e., Sn and Pb), Group VB metals (i.e., Sb and Bi) and Group VIIB metals (i.e., Mn, Tc and Re). The present catalyst may comprise one or more catalytic forms of one or more noble metals (i.e., Pt, Pd, Ir, Rh, Os or Ru). Combinations of catalytic forms of such noble or non-noble metals, such as combinations of Pt with Sn, may be used. The valence state of the metal of the hydrogenation/dehydrogenation component may be in a reduced valance state, e.g., when this component is in the form of an oxide or hydroxide. The reduced valence state of this metal may be attained, in situ, during the course of a reaction, when a reducing agent, such as hydrogen, is included in the feed to the reaction.

Other elements, such as alkali (Group IA) or alkaline earth (Group IIA) compounds may optionally be added to or co-precipitated with the present catalyst to alter catalytic properties. The addition of such alkali or alkaline earth compounds to the present catalyst may enhance the catalytic properties of components thereof, e.g., Pt or W, in terms of their ability to function as a hydrogenation/dehydrogenation component or an acid component.

The Group IVB metal (i.e., Ti, Zr or Hf) and the Group VIB metal (i.e., Cr, Mo or W) species of the present catalyst are not limited to any particular valence state for these species. These species may be present in this catalyst in any possible positive oxidation value for these species. Subjecting the catalyst, e.g., when the catalyst comprises tungsten, to reducing conditions, e.g., believed to be sufficient to reduce the valence state of the tungsten, may enhance the overall catalytic ability of the catalyst to catalyze certain reactions, e.g., the isomerization of n-hexane.

The modified acidic oxide may be contacted with hydrogen at elevated temperatures. These elevated temperatures may be 100°C or greater, e.g., 250°C or greater, e.g., about 300°C. The duration of this contact may be as short as one hour or even 0.1 hour. However, extended contact may also be used. This extended contact may take place for a period of 6 hours or greater, e.g., about 18 hours. When zirconia is modified with tungstate and then contacted with hydrogen at elevated temperatures, an increase in catalytic activity, e.g, for paraffin isomerization, has been observed. The modified acidic oxide may be contacted with hydrogen in the presence or absence of a hydrocarbon cofeed. For example, the activity of the catalyst may be increased, in situ, during the course of a reaction, such as hydrocracking, when a hydrocarbon and hydrogen are passed over the catalyst at elevated temperatures.

The optional hydrogenation/dehydrogenation component of the present catalyst may be derived from Group VIII metals, such as platinum, iridium, osmium, palladium, rhodium, ruthenium, nickel, cobalt, iron and mixtures of two or more thereof. Optional components of the present catalyst, which may be used alone or mixed with the above-mentioned hydrogenation/dehydrogenation components, may be derived from Group IVA metals, particularly Sn, and/or components derived from Group VIIB metals, particularly rhenium and manganese. These components may be added to the catalyst by methods known in the art, such as ion exchange, impregnation or physical admixture. For example, salt solutions of these metals may be contacted with the remaining catalyst components under conditions sufficient to combine the respective components. The metal containing salt may be water soluble. Examples of such salts include chloroplatinic acid, tetraammineplatinum complexes, platinum chloride, tin sulfate and tin chloride. The optional components may also be co-precipitated along with the other components of the modified oxide material.

When the present tungstate-modified zirconia catalyst is impregnated with platinum to form a catalyst particularly adapted to catalyze paraffin isomerization reactions, it has been discovered that it is desirable to co-precipitate about one percent by weight of Fe or Mn along with the solid precipitated from the aqueous mixture comprising the source of zirconia and the source of tungstate. Suitable iron salts, which may be included in this aqueous mixture, include $Fe(NO_3)_3$ and $Fe_2(SO_4)_3$.

The present modified oxide material may be recovered by filtration from the liquid medium, followed by drying.

Calcination of the resulting material may be carried out, particularly in an oxidizing atmosphere, at temperatures from about 500°C to about 900°C, particularly from about 700°C to about 850°C, and more particularly from about 750°C to about 825°C. The calcination time may be up to 48 hours, particularly for about 0.1-24 hours, and more particularly for about 1.0-10 hours. In an important embodiment, calcination is carried out at about 800°C for about 1 to about 3 hours. The optional components of the catalyst (e.g., Group VIII metal, Group VIIB metal, etc.) may be added after or before the calcination step by techniques known in the art, such as impregnation, co-impregnation, co-precipitation, physical admixture, etc. The optional components, e.g., the hydrogenation/dehydrogenation component, may also be combined with the remaining catalyst components before or after these remaining components are combined with a binder or matrix material as described hereinafter.

In the present catalyst, of the Group IVB oxides, zirconium oxide is important; of the Group VIB anions, tungstate is important; and of the optional hydrogenation/dehydrogenation components, platinum and/or platinum-tin are important.

Qualitatively speaking, elemental analysis of the present acidic solid will reveal the presence of Group IVB metal, Group VIB metal and oxygen. The amount of oxygen measured in such an analysis will depend on a number of factors, such as the valence state of the Group IVB and Group VIB metals, the form of the optional hydrogenation/dehydrogenation component, moisture content, etc. Accordingly, in characterizing the composition of the present catalyst, it is best not to be restricted by any particular quantities of oxygen. In functional terms, the amount of Group VIB oxyanion in the present catalyst may be expressed as that amount which increases the acidity of the Group IVB oxide. This amount is referred to herein as an acidity increasing amount. Elemental analysis of the present catalyst may be used to determine the relative amounts of Group IVB metal and Group VIB metal in the catalyst. From these amounts, mole ratios in the form of XO_2/YO_3 may be calculated, where X is said Group IVB metal, assumed to be in the form XO_2, and Y is said Group VIB metal, assumed to be in the form of YO_3. It will be appreciated, however, that these forms of oxides, i.e., XO_2 and YO_3, may not actually exist, and are referred to herein simply for the purposes of calculating relative quantities of X and Y in the present catalyst. The present catalysts may have calculated mole ratios, expressed in the form of XO_2/YO_3, where X is at least one Group IVB metal (i.e., Ti, Zr, and Hf) and Y is at least one Group VIB metal (i.e., Cr, Mo, or W), of up to 1000, e.g., up to 300, e.g., from 2 to 100, e.g., from 4 to 30.

The amount of iron and/or manganese which is incorporated into the present acidic solid may also be expressed in terms of calculated mole ratios of oxides, based upon the elemental analysis of the solid for the Group IVB metal, X, along with Mn and Fe. More particularly, this acidic solid may have a calculated mole ratio, expressed in terms of $XO_2/(MnO_2 + Fe_2O_3)$, of, for example, from 10 to 500. It will be appreciated, however, that Mn need not necessarily be in the form of MnO_2, and Fe need not be in the form of Fe_2O_3. More particularly, at least a portion of these components may be in the form of free metals or other combined forms than MnO_2 or Fe_2O_3 e.g., as salts with elements other than oxygen, in any possible valence state for X, Mn, or Fe. Accordingly, it will be understood that the expression, $XO_2/(MnO_2 + Fe_2O_3)$, is given merely for the purposes of expressing calculated quantities of X, Mn, and Fe, and is not to be construed as being limitive of the actual form of these elements in the present acidic solid material.

The amount of optional hydrogenation/dehydrogenation component may be that amount which imparts or increases the catalytic ability of the overall material to catalytically hydrogenate or dehydrogenate a hydrogenatable or dehydrogenatable organic compound under sufficient hydrogenation or dehydrogenation conditions. This amount is referred to herein as a catalytic amount. Quantitatively speaking, the present catalyst may comprise, for example, from about 0.001 to about 5 wt%, e.g., from about 0.1 to about 2 wt %, of the optional hydrogenation/dehydrogenation component, especially when this component is a noble metal.

Especially when the present catalyst includes a platinum hydrogenation/dehydrogenation component, this catalyst may also comprise up to about five weight percent of Fe and/or Mn, as measured by elemental analysis of the catalyst.

The present catalyst is acidic and may be observed as being highly acidic, even to the extent of being a superacid. Superacids are a known class of acidic materials which have an acidity greater than that of 100% H_2SO_4. This level of acidity may be determined by any appropriate means, including the use of suitable indicators, the determination of the ability to protonate certain chemicals, and/or the determination of the ability to stabilize certain cations, especially certain carbonium or carbenium ions. For example, this catalyst, whether analyzed in the presence or absence of optional components (e.g., hydrogenation/ dehydrogenation components) and/or binder materials, may have an acid strength of a superacid as measured by the color change of an appropriate indicator, such as the Hammett indicator. More particularly, the Ho acid strength of the present catalyst may have a value of less than -13, i.e., an "acid strength" of greater than -13. The use of Hammett indicators to measure the acidity of solid superacids is discussed in the

Soled et al. U.S. Patent No. 5,157,199. This Soled et al. patent also describes the Ho acid strength for certain sulfated transition metal superacids.

The catalyst described herein may be used as a catalyst for isomerizing C_4 to C_8 paraffins. Suitable feeds contain substantial amounts of normal and/or singly branched low octane C_4 to C_8 hydrocarbons. The feed may also contain appreciable amounts of C_6 and C_7 cyclic paraffins which may undergo ring-opening reactions.

The present isomerization process may be carried out by contacting the hydrocarbon feed in either liquid or gas phase with the solid catalyst at temperatures less than 500°C, particularly less than 350°C, particularly less than 300°C, and at pressure in the range from 1 to 200 atmospheres, particularly from 1 to 100 atmospheres, more particularly 5 to 50 atmospheres. The isomerization process may be carried out either in the presence or absence of hydrogen, especially in the presence of hydrogen. The mole ratio of hydrogen to hydrocarbon is particularly in the range of 0.01:1 to 10:1.

It may be desirable to incorporate the present catalyst with another material to improve its properties. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica, and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates, sols, or gels including mixtures of silica and metal oxides.

It is noted that the present catalyst need not contain any sulfate ion (U.S. Patent No. 4,918,041). It is believed that the present catalyst is more stable and also much easier to regenerate than sulfated catalysts, such as the superacid sulfated catalysts referred to in the aforementioned article by K. Arata and M. Hino in <u>Proceedings 9th International Congress on Catalysis</u>, Volume 4, pages 1727-1735 (1988).

In the present isomerization process, n-paraffinic and mono-methyl branched paraffinic components are isomerized to higher branched paraffins which are generally better octane boosters. By way of illustration, the significance of these reactions can be gleaned from a review of the following table of Octane Numbers of Pure Hydrocarbons from P.H. Emmett, ed., Catalysis, Vol. VI (1958).

Octane Numbers of Pure Hydrocarbons

Hydrocarbon	Blending Research Octane Number (clear)
Paraffins:	
n-heptane	0
2-methylhexane	41
3-methylhexane	56
2,2-dimethylpentane	89
2,3-dimethylpentane	87
2,2,3-trimethylbutane	113

The feedstock for the present process may be one which contains significant amounts of C_5+ normal and/or slightly branched paraffins. In addition, the feedstock may contain monocyclic aromatic compounds and/or cyclic paraffins, such as cyclohexane. Among the hydrocarbons having 6 or less carbon atoms in the feedstock, at least 1 wt.%, e.g., at least 5 wt.%, e.g., at least 10 wt.%, e.g., at least 20 wt.%, e.g., at least 30 wt.%, of these hydrocarbons may be cyclic hydrocarbons, e.g., aromatics or cyclic paraffins.

The present catalyst may be used to isomerize C_4-C_8 paraffin hydrocarbons, either as pure compounds or mixtures. In refinery operations, the paraffins will normally be present in mixtures and, in addition to the C_4-C_8 materials, may contain hydrocarbons boiling outside this range; cycloparaffins and aromatics may also be present. Thus, the feed will comprise C_4-C_8 paraffins such as butane, pentane, hexane and these may be present in refinery streams such as raffinate cuts from solvent extraction units, reformer feedstock or pyrolysis gasoline from ethylene crackers. The feeds may also contain cyclic hydrocarbons, e.g., in the form of C_6+ naphthas; the cyclic materials in such feeds may undergo ring opening reactions in the presence of the catalyst with its associated metal component, to form paraffins which then undergo isomerization to iso-paraffins which can be separated from the cyclics by fractionation with the cyclics being recycled to extinction. In addition to pure paraffin feeds (C_4-C_8), mixed paraffin-olefin feeds containing significant levels of olefin may be utilized.

The isomerization is carried out in the presence of the catalyst, particularly in the presence of hydrogen. Reaction temperatures are suitably in the range of 200 to 800°F (93 to 425°C); temperatures outside this range may be utilized although they are normally less typical; temperatures from 300 to 700°F (149 to 370°C) are typical. Pressures will normally be up to 1000 psig (7,000 kPa abs.) although there is no reason why higher pressures should not be utilized. Lower pressures, in the range of 50 to 600 psig (445 to 790 kPa abs.) may readily be employed and the use of relatively low pressures within this range will generally be preferred in order to permit the use of low pressure equipment. The isomerization is usually carried out in the presence of hydrogen, typically at a molar ratio relative to the feed from 0.01 to 10:1 and usually from 0.5:1 to 2:1. Space velocities are typically from 0.1 to 10 LHSV and usually from 0.5 to 5 LHSV. When an additional acidic material (Lewis acid or Brønsted acid) is included in the catalyst, lower operational temperatures may be used, favoring the isomerization over the less desired cracking reactions.

The optional noble metal component of the present catalyst provides a hydrogenation-dehydrogenation component to the catalyst. Metals having a strong hydrogenation function are preferred, especially platinum and the other noble metals such as palladium, rhodium, iridium, rhenium, although other metals capable of acting as a hydrogenation component may also be used, for example, nickel, tungsten or other metals of Group VIII, either singly, in mixtures or in combination with other metals. The amount of the noble metal component may be in the range 0.001 to 5 wt.% of the total catalyst, e.g., from 0.1 to 2 wt. %. Base metal hydrogenation components may be added in somewhat greater amounts. The hydrogenation component can be exchanged onto the support material, impregnated into it or physically admixed with it. If the metal is to be impregnated into or exchanged onto the support, it may be done, for example, by treating the support with a platinum metal-containing ion. Suitable platinum compounds include chloroplatinic acid, platinous chloride and various compounds containing the platinum ammine complex. The metal compounds may be either compounds in which the metal is present in the cation or anion of the compound; both types of compounds can be used. Platinum compounds in which the metal is in the form of a cation of cationic complex, e.g., $Pt(NH_3)_4Cl_2$ are particularly useful, as are anionic complexes such as the vanadate and metatungstate ions. Cationic forms of other metals are also useful since they may be exchanged onto the support or impregnated into it.

The catalyst may be subjected to a final calcination under conventional conditions in order to dehydrate the catalyst and to confer the required mechanical strength on the catalyst. Prior to use the catalyst may be subjected to presulfiding.

When a source of hydrogenation metal, such as H_2PtCl_6, is used as a source of a hydrogenation/dehydrogenation component in the present catalyst, it may be desirable to subject the present catalyst to extended reducing conditions, e.g., lasting more than 4 hours.

Higher isomerization activity may be provided by the inclusion of an additional material having Lewis or Brønsted acid activity in the catalyst, especially when the catalyst comprises a porous binder material. For this purpose, both liquid and solid acid materials may be used. Examples of suitable additional acidic materials include aluminum trichloride, boron trifluoride and complexes of boron trifluoride, for example, with water, lower alcohols or esters. The maximum amount which may be added is set by the ability of the support material, especially the binder material, to sorb the added component and is readily determined by experiment.

The present catalyst may be used as the exclusive isomerization catalyst in single or multiple catalyst beds or it may be used in combination with other isomerization catalysts. For example, a feed may be first contacted with a catalyst bed comprising the present catalyst followed by contact with a second catalyst bed comprising a different catalyst, such as Pt on mordenite, Pt on zeolite beta or a chlorided platinum-alumina catalyst, as described in U.S. Patent Nos. 4,783,575 and 4,834,866. The temperature of the first catalyst bed may be higher than the temperature of the second catalyst bed. When the present catalyst is called upon to cause extensive ring opening, especially in an initial catalyst bed, relatively high temperatures, e.g., as high as 500°C, and/or relatively high pressures, e.g., as high as 200 atmospheres, may be employed.

The present catalyst can be shaped into a wide variety of particle sizes. Generally speaking, the particles can be in the form of a powder, a granule, or a molded product, such as an extrudate having particle size sufficient to pass through a 2 mesh (Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion, the catalyst can be extruded before drying or partially dried and then extruded. The present catalyst may be composited with a matrix material to form the finished form of the catalyst and for this purpose conventional matrix materials such as alumina, silica-alumina and silica are suitable with preference given to silica when a non-acidic binder is desired. Other binder materials may be used, for example, titania, zirconia and other metal oxides or clays. The active catalyst may be composited with the matrix in amounts from 80:20 to 20:80 by weight, e.g., from 80:20 to 50:50 active catalyst:matrix. Compositing may be done by conventional means including mulling the materials together followed by extrusion of pelletizing into the desired finished catalyst particles.

The catalyst may be treated by conventional presulfiding treatments, e.g., by heating in the presence of hydrogen sulfide, to convert oxide forms of the metal components to their corresponding sulfides.

Although the use of the present catalyst in isomerization reactions has been emphasized hereinabove, it will be appreciated that this catalyst is useful for a variety of organic, e.g., hydrocarbon, compound conversion processes. When the present catalyst comprises a hydrogenation/dehydrogenation component, it may be used in reactions requiring the use of a dual-functional (1) acidic and (2) hydrogenation/dehydrogenation catalyst. Such conversion processes include, as non-limiting examples, hydrocracking hydrocarbons with reaction conditions including a temperature of from 100°C to 700°C, a pressure of from 0.1 atmosphere (bar) (10 KPa) to 30 atmospheres (3040 KPa), a weight hourly space velocity of from 0.1 to 20, and a hydrogen/ hydrocarbon mole ratio of from 0 to 20; dehydrogenating hydrocarbon compounds with reaction conditions including a temperature of from 300°C to 700°C, a pressure of from 0.1 atmosphere (10 KPa) to 10 atmospheres (1013 KPa) and a weight hourly space velocity of from 0.1 to 20; converting paraffins to aromatics with reaction conditions including a temperature of from 100°C to 700°C, a pressure of from 0.1 atmosphere (10 KPa) to 60 atmospheres (6080 KPa), a weight hourly space velocity of from 0.5 to 400 and a hydrogen/hydrocarbon mole ratio of from 0 to 20; converting olefins to aromatics, e.g., benzene, toluene and xylenes, with reaction conditions including a temperature of from 100°C to 700°C, a pressure of from 0.1 atmosphere (10 KPa) to 60 atmospheres (6080 KPa), a weight hourly space velocity of from 0.5 to 400 and a hydrogen/ hydrocarbon mole ratio of from 0 to 20; transalkylating aromatic hydrocarbons in the presence of polyalkylaromatic hydrocarbons with reaction conditions including a temperature of from 100°C to 500°C, a pressure of from atmospheric (101 KPa) to 200 atmospheres (20265 KPa), a weight hourly space velocity of from 10 to 1000 and an aromatic hydrocarbon/polyalkylaromatic hydrocarbon mole ratio of from 0.3/1 to 20/1, and a hydrogen/hydrocarbon mole ratio of from 0 to 20; and transferring hydrogen from paraffins to olefins with reaction conditions including a temperature from -25°C to 400°C, e.g., from 75°C to 200°C, a pressure from below atmospheric (101 KPa) to 5000 psig (34566 KPa), e.g., from atmospheric (101 KPa) to 1000 psig (6994 KPa), a mole ratio of total paraffin to total olefin of from 1:2 to 500:1, e.g., from 5:1 to 100:1; and a weight hourly space velocity based on olefin of from 0.01 to 100, e.g., from 0.05 to 5.

The present catalyst may also be used in an isoparaffin/ olefin alkylation process. The isoparaffin may be isobutane and the olefin may be ethylene, propylene and/or butene(s), e.g., 2-butene. The isoparaffin/olefin alkylation reaction may take place in the presence or absence of a hydrogenation/ dehydrogenation component, in the presence or absence of cofed hydrogen, at a temperature of from -25°C to 400°C with 75°C being a more useful upper limit, at a pressure from below atmospheric (101 KPa) to 5000 psig (34566 KPa), at a weight hourly space velocity based on olefin of from 0.01 to 100 hr^{-1}, and at a mole ratio of total isoparaffin to total olefin of from 1:2 to 500:1.

The present catalyst may also be used in various hydroprocessing reactions, such as the removal of metals, nitrogen and/or sulfur from feedstocks, such as resids, including such elements, particularly in the form of heteroatoms. These hydroprocessing reactions comprise contacting the feedstock along with a sufficient amount of hydrogen with the present catalyst under conditions sufficient to remove metals, nitrogen, and/or sulfur.

Example 1

This Example describes the preparation of a tungstate-modified zirconia (WO_x/ZrO_2). Five hundred grams of $ZrOCl_2 \cdot 8H_2O$ were dissolved with stirring in 7.0 liters of distilled H_2O. A solution containing 263 ml of conc. NH_4OH, 500 mL of distilled H_2O, and 54 grams of $(NH_4)_6H_2W_{12}O_{40} \cdot x H_2O$ was added dropwise over a 30-45 minute period. The pH of the solution was adjusted to approximately 9 (if needed) by adding additional conc. NH_4OH dropwise. This slurry was then placed in the steambox for 72 hours. The product formed was recovered by filtration, washed with excess H_2O, and dried overnight at 85°C. The material was then calcined in dry air to 825°C for 3 hours.

EXAMPLE 2

This Example describes the preparation of a tungstate-modified zirconia containing 0.6 wt.% Pt (0.6 wt.% $Pt/WO_x/ZrO_2$). Twelve grams of WO_x/ZrO_2, prepared according to Example 1, were impregnated with a solution containing 0.19217 grams of $H_2PtCl_6 \cdot 6H_2O$ dissolved in 20 ml of distilled deionized H_2O by incipient wetness. The resulting catalyst was dried and then calcined at 300°C in dry air for 2 hours.

EXAMPLE 3

This Example describes the preparation of 0.3 wt.% $Pt/WO_x/ZrO_2$. Twelve grams of WO_x/ZrO_2, prepared according to Example 1, were impregnated with a solution containing 0.096 grams of $H_2PtCl_6 \cdot 6H_2O$ dissolved in 20 ml of distilled deionized H_2O by incipient wetness. The resulting catalyst was dried and then calcined at 300°C in dry air for 2 hours.

EXAMPLE 4

This Example describes the preparation of 0.5 wt.% $Pt/SiO_2\text{-}WO_x/ZrO_2$. Twelve grams of WO_x/ZrO_2, prepared according to Example 1, were mechanically mixed with 7 grams of a 0.5 wt.% Pt/SiO_2 catalyst. The 0.5 wt.% Pt/SiO_2 catalyst was prepared via ion exchange. Silica gel (Davison Chemical, Grade 12) was exchanged with an aqueous solution containing $Pt(NH_3)_4^{++}$ under basic conditions, pH ~9. The resulting material was dried at 120°C for 16 hours and then air calcined at 350°C for 4 hours. The 0.5 wt.% Pt/SiO_2 catalyst was cooled to room temperature before reduction in flowing hydrogen at 450°C for 30 minutes.

EXAMPLE 5

This Example describes the preparation of $Fe/Mn/WO_x/ZrO_2$. Five hundred grams of $ZrOCl_2 \cdot 8H_2O$ were dissolved with stirring in 6.5 liters of distilled H_2O. A solution containing 4.6 grams of $MnSO_4 \cdot H_2O$ and 7.6 grams of $FeSO_4 \cdot 7H_2O$ dissolved in 500 ml of distilled H_2O was then added to the zirconyl-containing solution. A third solution containing 263 mL of conc. NH_4OH, 500 mL of distilled H_2O, and 54 grams of $(NH_4)_6H_2W_{12}O_{40} \cdot x\ H_2O$ was added dropwise over a 30-45 minute period to the iron/manganese/zirconium mixture. The pH of the solution was adjusted to approximately 9 (if needed) by adding additional conc. NH_4OH dropwise. This slurry was then placed in the steambox for 72 hours. The product formed was recovered by filtration, washed with excess H_2O, and dried overnight at 85°C. The material was then calcined in dry air to 825°C for 3 hours.

EXAMPLE 6

Twelve grams of $Fe/Mn/WO_x/ZrO_2$, prepared according to Example 5, were impregnated with a solution containing 0.19217 grams of $H_2PtCl_6 \bullet 6H_2O$ dissolved in 20 ml of distilled deionized H_2O by incipient wetness. The resulting catalyst was dried and then calcined at 300°C in dry air for 2 hours.

EXAMPLE 7

This Example describes the preparation of $Fe/WO_x/ZrO_2$. Five hundred grams of $ZrOCl_2 \bullet 8H_2O$ were dissolved with stirring in 6.5 liters of distilled H_2O. A solution containing 7.5 grams of $FeSO_4 \bullet 7H_2O$ dissolved in 500 ml of distilled H_2O was then added to the zirconyl-containing solution. A third solution containing 263 mL of conc. NH_4OH, 500 mL of distilled H_2O, and 54 grams of $(NH_4)_6H_2W_{12}O_{40} \bullet x\ H_2O$ was added dropwise over a 30-45 minute period to the iron/zirconium mixture. The pH of the solution was adjusted to approximately 9 (if needed) by adding additional conc. NH_4OH dropwise. This slurry was then placed in the steambox for 72 hours. The product formed was recovered by filtration, washed with excess H_2O, and dried overnight at 85°C. The material was then calcined in dry air to 825°C for 3 hours.

EXAMPLE 8

This Example describes the preparation of Pt-containing $Fe/WO_x/ZrO_2$. Thirty-six grams of $Fe/WO_x/ZrO_2$, prepared according to Example 7, were impregnated with a solution containing 0.58 grams of $H_2PtCl_6 \bullet 6H_2O$ dissolved in 60 ml of distilled deionized H_2O by incipient wetness.

The resulting catalyst was dried and then calcined at 300°C in dry air for 2 hours.

EXAMPLE 9

This Example describes the preparation of $Mn/WO_x/ZrO_2$. Five hundred grams of $ZrOCl_2 \bullet 8H_2O$ were dissolved with stirring in 6.5 liters of distilled H_2O. A solution containing 4.6 grams of $MnSO_4 \bullet 7H_2O$ dissolved in 500 ml of distilled H_2O was then added to the zirconyl-containing solution. A third solution containing 263 mL of conc. NH_4OH, 500 mL of distilled H_2O, and 54 grams of $(NH_4)_6H_2W_{12}O_{40} \bullet x\ H_2O$ was added dropwise over a 30-45 minute period to the manganese/zirconium mixture. The pH of the solution was adjusted to approximately 9 (if needed) by adding additional conc. NH_4OH dropwise. This slurry was then placed in the steambox for 72 hours. The product formed was recovered by filtration, washed with excess H_2O, and dried overnight at 85°C. The material was then calcined in dry air to 825°C for 3 hours.

EXAMPLE 10

This Example describes the preparation of Pt-containing $Mn/WO_x/ZrO_2$. Twelve grams of $Mn/WO_x/ZrO_2$, prepared according to Example 9, were impregnated with a solution containing 0.1926 grams of $H_2PtCl_6 \bullet 6H_2O$ dissolved in 20 ml of distilled deionized H_2O by incipient wetness. The resulting catalyst was dried and then calcined at 300°C in dry air for 2 hours.

EXAMPLES 11-14

These Examples illustrate the adverse effect of Pt on the activity of WO_x/ZrO_2 for pentane isomerization. Catalysts of Examples 1-4 were tested for pentane isomerization activity in a fixed-bed down-flow reactor at 210°C, 350 psig, 2 mol H_2/mol $n-C_5$, and 2 LHSV (cc $n-C_5$ feed per cc catalyst per hour). The catalysts were calcined at

300°C for 1 hour under flowing nitrogen prior to catalytic testing. The results are shown in Table 1. The adverse effect of Pt on the activity of the WO_x/ZrO_2 catalyst is apparent when comparing the activity of the Pt-free WO_x/ZrO_2 catalyst, column 1, with that of the Pt-containing WO_x/ZrO_2 catalysts, columns 2 through 4. The activity of the Pt-containing catalysts was less than the Pt-free version.

EXAMPLES 15-18

These Examples illustrate the beneficial effect of Pt on the activity and selectivity of $Fe/Mn/WO_x/ZrO_2$ catalyst for pentane isomerization. Catalysts of Examples 5-10 were tested for pentane isomerization activity at conditions similar to those described in Examples 11-14. The results are shown in Table 2. Columns 1 and 2 present the results obtained over Pt-free $Fe/Mn/WO_x/ZrO_2$ at two different temperatures, 200°C and 210°C. The results over the Pt-containing $Fe/Mn/WO_x/ZrO_2$ at 200°C and 210°C are shown in columns 3 and 4, respectively. With the addition of the Fe/Mn, the Pt-containing catalyst maintained high activity.

EXAMPLES 19-20

These Examples illustrate the activity of $Pt/Fe/WO_x/ZrO_2$ and $Pt/Mn/WO_x/ZrO_2$ for pentane isomerization. Catalysts of Examples 8 and 10 were tested for pentane isomerization activity at conditions similar to those described in Examples 11-14. The results are presented in Table 3. The beneficial effect of adding Fe or Mn to maintain the high activity of WO_x/ZrO_2 catalyst upon addition of Pt is apparent when comparing columns 2 through 4 of Table 1 with columns 1 and 2 of Table 3.

EXAMPLES 21-22

These Examples describe n-hexane isomerization over Pt-free $Fe/WO_x/ZrO_2$ and Pt-containing $Fe/WO_x/ZrO_2$. Catalysts of Examples 7 and 8 were tested for n-hexane isomerization at 210°C, 450 psig, 2 mol H_2/mol n-C_6, and 2 LHSV (cc n-C_5 feed per cc catalyst per hour). The results are shown in Table 4. It is apparent that addition of Pt to the Fe/WO_x/ZrO_2 improves both the n-hexane isomerization activity and the selectivity to the desirable high-octane dimethyl butanes.

Table 1
n-Pentane Isomerization Data from Examples 11-14

Example	11	12	13	14
		Pt/	Pt/WO_x/	
Pt/SiO_2/				
Catalyst	WO_x/ZrO_2	WO_x/ZrO_2	ZrO_2	WO_x/ZrO_2
Catalyst preparation given in Example	1	2	3	4
Product Dist., wt.%				
C_1 +C_2	0.4	0.1	0.1	0.2
C_3	0.4	0.1	0.2	0.2
i-C_4	2.7	0.1	---	0.3
n-C_4	0.2	0.1	0.1	0.1
i-C_5	69.1	52.4	46.9	40.4
n-C_5	26.5	47.1	52.7	58.6
C_6+	0.6	0.2	0.05	0.9
n-C_5 conv., wt.%	73.5	52.9	47.3	41.4
i-C_5/total C_5, %	72.3	52.7	47.1	40.8

Table 2

n-Pentane Isomerization Data from Examples 15-18

Example	15	16	17	18
	Fe/Mn/	Fe/Mn/	Pt/Fe/Mn/	
Pt/Fe/Mn/ Catalyst WO_x/ZrO_2		WO_x/ZrO_2	WO_x/ZrO_2	WO_x/ZrO_2
Catalyst preparation given in Example	5	5	6	6
Operating temp., °C	200	210	200	210
Product Dist., wt.%				
$C_1 + C_2$	0.7	1.0	0.4	0.5
C_3	0.5	0.8	0.4	0.5
i-C_4	1.3	2.5	0.2	0.3
n-C_4	0.2	0.3	0.3	0.5
i-C_5	64.6	68.6	70.8	70.9
n-C_5	32.7	26.6	27.5	26.7
C_6+	---	0.2	0.3	0.5
n-C_5 conv., wt.%	67.3	73.4	72.5	73.3
i-C_5/total C_5, %	66.4	72.0	72.0	72.6

Table 3

n-Pentane Isomerization Data from Examples 19 and 20

Example	19	20
Catalyst	Pt/Fe/ WO_x/ZrO_2	Pt/Mn/ WO_x/ZrO_2
Catalyst preparation given in Example	8	10
Product Dist., wt.%		
C_1 +C_2	0.7	0.1
C_3	0.8	0.3
i-C_4	0.7	0.2
n-C_4	0.9	0.2
i-C_5	69.3	69.4
n-C_5	26.8	29.3
C_6+	0.8	0.4
n-C_5 conv., wt.%	73.2	70.7
i-C_5/total C_5, %	72.1	70.3

Table 4

Hexane Isomerization Data from Examples 21 and 22

Example	21	22
Catalyst	Fe/ WO_x/ZrO_2	Pt/Fe/ WO_x/ZrO_2
Catalyst preparation given in Example	7	8
Product Dist., wt.%		
$C_1 + C_2$	0.03	0.6
C_3	1.3	1.2
$i-C_4$	9.3	0.9
$n-C_4$	0.9	0.9
$i-C_5$	5.6	1.0
$n-C_5$	0.9	0.4
2,2-dimethyl butane	5.3	24.4
2,3-dimethyl butane	9.0	9.1
2-methyl pentane	30.0	29.6
3-methyl pentane	18.6	18.2
n-hexane	18.4	13.4
C_7+	tr	tr
n-hexane conv., wt.%	81.6	86.6
Dimethyl butanes yield, wt.%	14.3	33.5

What is claimed is:

1. An acidic solid comprising a Group IVB metal oxide modified with an oxyanion of a Group VIB metal, said acidic solid further comprising an oxide of at least one metal selected from the group consisting of iron and manganese.

2. An acidic solid according to claim 1 further comprising a noble metal.

3. An acidic solid according to claim 2, wherein said noble metal is platinum.

4. A method for preparing an acidic solid comprising a Group IVB metal oxide modified with an oxyanion of a Group VIB metal, said method comprising co-precipitating a source of a Group IVB metal oxide, a source of an oxyanion of a Group VIB metal, and a source of an oxide selected from the group consisting of Fe and Mn.

5. A method according to claim 4, wherein the source of said oxyanion of a Group VIB metal is selected from the group consisting of ammonium metatungstate, ammonium metamolybdate, tungsten chloride, molybdenum chloride, tungsten carbonyl, molybdenum carbonyl, tungstic acid, sodium tungstate, and sodium molybdate.

6. A method according to claims 1 or 4, wherein said Group IVB metal is Zr and wherein said Group VIB metal is W.

7. A method for preparing an acidic solid comprising tungstate-modified zirconia, said method comprising the steps of:

(a) combining a first liquid solution with a second liquid solution and a third liquid solution, said first solution comprising a source of zirconia dissolved in water, said second solution comprising a source of tungstate dissolved in water, and said third solution comprising a source of at least one oxide selected from the group consisting of iron and manganese;

(b) maintaining the combined solutions of step (a) under conditions sufficient to form a solid co-precipitate comprising tungstate-modified zirconia and at least one compound comprising Fe and/or Mn;

(c) recovering the solid co-precipitate from step (b) by filtration; and

(d) calcining the recovered co-precipitate from step (c).

8. A method according to claim 7, wherein said source of zirconia is $ZrOCl_2$ and said source of tungstate is ammonium metatungstate.

9. A process for converting an organic compound, said process comprising contacting said organic compound with a catalyst under sufficient conversion conditions, wherein said catalyst comprises an acidic solid comprising a Group IVB metal oxide modified with an oxyanion of a Group VIB metal, said acidic solid further comprising an oxide of at least one metal selected from the group consisting of iron and manganese.

10. A process for isomerizing hydrocarbons, said process comprising contacting a feed comprising C_4 to C_8 hydrocarbons with an isomerization catalyst under sufficient isomerization conditions, said isomerization catalyst comprising (i) a noble metal and (ii) an acidic solid comprising a Group IVB metal oxide modified with an oxyanion of a Group VIB metal, said acidic solid further comprising an oxide of at least one metal selected from the group consisting of iron and manganese.

11. A process according to claim 10, wherein said noble metal comprises platinum.

12. A process according to claim 10, wherein said Group IVB metal oxide comprises zirconia or titania and said Group VIB metal oxyanion is an oxyanion of molybdenum or tungsten.

13. A process according to claim 10, wherein said noble metal comprises platinum in the form of an oxide, hydroxide or free metal, said Group IVB metal oxide is zirconium oxide, and said Group VIB metal oxyanion is tungstate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/14712

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 23/00; C07C 5/13, 5/22, 5/23, 5/25
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/305, 308, 309, 313, 316, 349, 350; 585/664, 671, 670, 700, 734, 750

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A 5,019,671 (Hsu et al.) 28 May 1991, see column 2, lines 1-16, column 2, lines 25-40 and column 3, lines 12-21.	ALL
Y,P	US,A 5,396,011 (Kuhn) 07 March 1995, see column 3, lines 27-56	1-8
X	Journal Chem. Soc. Chem. Commun., 1988, Hino et al., "Synthesis of Solid Superacid of Tungsten Oxide Supported on Zirconia and its Catalytic Action for Reactions of Butane and Pentane", pages 1259-1260, especially the third paragraph.	ALL

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search

26 JANUARY 1996

Date of mailing of the international search report

23 FEB 1996

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/14712

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Proceedings 9th International Congress on Catalysis, Vol. 4, Oxide Catalysts and Catalyst Development, (1988) Arata et al., "Synthesis of Solid Superacid of Tungsten Oxide Supported on Zirconia and its Catalytic Action", pages 1727-1734, especially page 1730	ALL

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/14712

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

502/305, 308, 309, 313, 316, 349, 350; 585/664, 671, 670, 700, 734, 750