The improved, heterogeneous catalysts are in the form of gas-impermeable, hollow, thin-walled spheres (10) suitably formed of a shell (12) of metal such as aluminum having a cavity (14) containing a gas at a pressure greater than atmospheric pressure. The wall material may be, itself, catalytic or the catalyst can be coated onto the sphere as a layer (16), suitably platinum or iron, which may be further coated with a layer (18) of activator or promoter. The density of the spheres (30) can be uniformly controlled to a preselected value within ±10 percent of the density of the fluid reactant such that the spheres either remain suspended or slowly fall or rise through the liquid reactant.

5 Claims, 6 Drawing Figures
CATALYTIC HOLLOW SPHERES

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 83-568 (72 Stat. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

The present invention relates to heterogeneous catalysts and more particularly, this invention relates to hollow, gas-impervious, catalytic spheres having a pre-selected density for the controlled and uniform conversion of catalytically reactive fluid materials.

STATEMENT OF THE PRIOR ART

The relative merits of homogeneous and heterogeneous catalysts are well known. Homogeneous catalysts have better defined active sites, usually have all of the metal available for catalysts, and offer steric and electronic environments of the metal atom that can, at least in principle, be varied at will. The major disadvantage of homogeneous catalysts is the need to separate them from reaction products without loss of their valuable metal content. This step can be both complex and expensive. Other disadvantages are that these catalysts are relatively easily deactivated through aggregation or by poisonous by-products at extreme temperatures. Also, corrosion of reactors by metal complexes is common.

Heterogeneous catalytic processes are of great industrial importance. Annually, 10,000 metric tons of ammonia are produced by direct combination of nitrogen and hydrogen gases at 400° C. and high pressure over iron catalysts promoted by several percent K2O and Al2O3. Large volumes of sulfuric acid and methanol are also produced by heterogeneous catalysis. About 70 percent of all petrochemicals and refined petroleum products are produced by heterogeneous catalytic processes. Hydrogenation in presence of noble metals such as platinum or palladium or transition metals such as nickel or cobalt can be used to convert carbon monoxide to many different products such as ketones or alcohols. Also, conversion of olefins to alkanes, benzene to cyclohexane or nitro groups to amine groups. Transition metal catalysts also show activity for a wide variety of industrially important reactions such as isomerization, hydroformylation, carbonylation, etc. These catalysts can be used to convert pyrolysis coal gases into synthetic fuels such as oxo alcohols.

Heterogeneous catalysts have been developed in which the homogeneous catalyst is either impregnated onto or chemically bonded to a solid support. Reaction rate is also dependent on surface area, and many catalysts are provided in finely divided form such as fine powders of platinum prepared by reduction of the oxide. Catalysts are also prepared by impregnating the active catalyst onto high area supports, for example, platinum deposited onto alumina particles having surface areas of the order of 100 square meters per gram. Heterogeneous catalysts have been prepared by coating the catalyst onto a hollow, porous support.

Baer, et al. (U.S. Pat. No. 3,347,798) prepare hollow, catalytic beads having a diameter greater than 90 microns for a fluidized bed process. The beads are gas-permeable so that reactants can diffuse into the core and react with the inner wall. The beads are formed by spraying a hydrogel such as silicic acid or alumina containing a vaporizable expanding agent through a nozzle into a tower and impinging the stream with a gas heated to 300°-700° C. Fitch, et al. (U.S. Pat. No. 3,538,018) disclose an improvement over Baer, et al., in which compact catalyst particles are added to the hollow spheres to form a mixture having a controlled density. Ao (U.S. Pat. No. 3,798,176) manufactures controlled-density, catalyst pellets having a vacant or a dense center. Ao forms a vacant center pellet; a thin polymeric shell is coated with a carrier and catalyst particles. During calcination, the core burns away and the particles sinter and consolidate into a gas-permeable shell. In the dense center pellet, the core is made by pelletizing a ceramic. Martin (U.S. Pat. No. 3,978,269) forms porous pellets for automotive exhaust reactors by coating liquid droplets with a powder mixture of ceramic and binder and then firing to form a porous, breathable, hollow pellet. Watson, et al. (U.S. Pat. No. 4,039,480) also form an automotive catalyst by coating a dry core with a dispersion of ceramic and firing to form a product having a bulk density below 50 lbs/ft3. Barnes, Jr. (U.S. Pat. No. 4,292,206) incorporates tiny, hollow glass spheres in the alumina powder mix as a lightweight filler to reduce weight of the resultant catalyst beads. These porous catalystic particles are not uniformly dispersed in the fluid reaction media. They require separation of the reactant and product from the catalyst. The ceramic or polymer supported catalyst particles tend to crack, corrode or decay, which clogs the catalyst bed and requires shutting the reactor down to replace the bed and incurs the expense of replacing the catalyst. Irregularly-shaped catalysts are not an optimum shape for catalytic reaction kinetics. The metal catalyst is heavy and would sink to the bottom of the reactor unless the reaction media is stirred or the catalyst circulated through it.

STATEMENT OF THE INVENTION

Improved heterogeneous catalysts are provided in accordance with the present invention. The catalysts of the invention have a uniform, controlled density that can be preselected such that the spheres disperse uniformly throughout a fluid reaction medium or rise or fall through the medium at a preselected rate. The catalyst particles of the invention are very strong and physically tough and will not crack, chip or abrade. The particles can be used and reused for numerous runs before requiring any regeneration or reprocessing. The catalyst of the invention provides a large surface area for optimum contact of reagent and catalyst while assuring unobstructed flow of reactants through the bed of catalyst.

The catalyst of the invention automatically distributes through the reagent or can flow through the body of reagent without requiring shaking, stirring or pumping. The catalyst particles are readily prepared in large volume and uniform shape at low cost by the process of the invention.

The improved catalyst provided by the present invention is in the form of gas-impervious, hollow, thin-walled spheres. The wall material may itself be catalytic or the catalyst can take the form of a coating onto the wall material. Additional layers of activators or promoters can be coated onto the sphere or the promoters or activators can be mixed into the layer of catalyst. The
density of the spheres can be accurately controlled by
controlling the internal gas pressure and/or wall thick-
ness of the spheres to form a uniform batch of spheres
in which the weight of the spheres varies less than ± 5
percent.

Spheres that are from 0.5 to 10 percent by weight
lighter than the reaction media will slowly rise at a
controlled rate through the reaction media. Spheres
that have substantially the same density (±0.01 to 0.5
percent by weight) as the reaction media will remain
uniformly dispersed therein and spheres that are from
0.5 to 10 percent heavier than the reaction media will
slowly fall through the media. The spheres can be pro-
duced over a fairly large range in diameter, such as
from 0.20 to 5.0 millimeters and still provide sufficient
surface area for the catalytic reaction to proceed at an
economic rate.

The spherical catalysts are readily dispersed with a
minimal amount of energy and can reject exothermic
heat to the surrounding reaction media. The catalyst
of the invention is easy to handle and readily separates
from the reaction media for cleaning, reprocessing,
regeneration or recirculation. There is no problem with
packed beds or with fluid flow since the catalyst spheres
maintain a uniform dispersion with separation between
adjacent layers. The catalyst spheres of the invention
provide optimum utilization of expensive catalyst materials
since the catalyst materials are provided on the surface.

The inner, inert core of the particles is filled with inert
gas. The catalysts of the invention are applicable for all
prior heterogeneous reactions such as hydrogenation,
polymerization or oligomerization, isomerization, etc.

These and many other features and attendant advan-
tages of the invention will become apparent as the in-
vention becomes better understood by reference to the
following detailed description when considered in con-
junction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a catalyst sphere
according to the invention;

FIG. 2 is a schematic view of a batch reactor contain-
ing a uniform dispersion of catalyst spheres;

FIG. 3 is a schematic view of a fluidized bed reactor
containing a bed of catalyst spheres;

FIG. 4 is a schematic view of a reactor with a falling
column of catalyst spheres;

FIG. 5 is a schematic view of a reactor with a rising
column of catalyst spheres; and

FIG. 6 is a schematic view of a continuous flow reac-
tor with continuous circulation of catalyst and continu-
ous introduction of reactant and removal of reaction
product.

DETAILED DESCRIPTION OF THE
INVENTION

Referring now to FIG. 1, the catalyst of the invention
is in the form of a hollow sphere 10 having a gas-imper-
vious shell 12 formed of a metal. The hollow, interior
cavity 14 contains a gas such as air under pressure. The
presence of the gas and the thickness and weight of the
shell and any promoter or initiator layers thereon are
selected to provide a predetermined density in relation
to the density of the fluid reaction media. The shell may
be formed of a catalytically active metal such as plati-
num or iron or may be formed of another metal such as
aluminum or bronze. The catalyst layer 16 of catalyst, e.g.,
platinum or iron. The catalyst layer 16 may be from 0.1
μm to 0.1 mm in thickness. The catalyst layer 16 may
contain from 1 to 25 percent by weight of a promoter
initiator such as an alkali metal oxide, or a thin layer 18
from 0.1 μm to 0.1 mm in thickness of the promoter, or
the initiator may be coated onto the surface of the cata-
lyst layer. The layers 16, 18 may be formed by deposi-
tion of the compounds from the vapor or liquid phase
such as by thermal decomposition of metal carbonyls
and the like.

Gas-filled, spherical, metal shells, that are dimension-
ally precise, smooth and of high strength can be pro-
duced by a method based on the hydrodynamic instabil-
ity of an annular jet of molten metal as disclosed in U.S.
Pat. No. 4,344,787, the disclosure of which is expressly
incorporated herein by reference. The basis of the
method rests upon the phenomenon of instability and
breakup of a jet flow of liquid as it issues into a gaseous
medium at rest. In the embodiment employed herein, a
coaxial flow of fill gas is provided at the core of a circu-
lar jet by means of a thin-wall tube. When the axial
velocities of the jet liquid and of the central gas are
adjusted to fall within certain ranges, the jet exhibits an
instability which generates large-amplitude axisymmet-
ric oscillations. These culminate in a rapid pinchoff
of the jet and in the formation of liquid shells which can be
described as thin-shell bubbles. The oscillation growth is
so rapid that the nonlinear

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pressure of about 100 psi could be coated with a 0.1 µm thick layer of platinum by reduction of precursor oxide powder. Palladium or nickel could also be coated onto the aluminum shell by this technique. These catalysts could be utilized for hydrogenation reactions. When the aluminum shell is coated with iron, the spheres can be utilized to produce ammonia by combining N₂ and H₂ gases at 400° C. and several hundred atmospheres of pressure. Further coating the iron layer with a layer of Na₂O or K₂O results in a synthesis gas conversion catalyst which converts CO and H₂ gases into product gas containing CH₄, C₂H₆, C₃H₈, C₄H₁₀, other alkanes, olefinics, aldehydes and acids.

The ability to adjust the buoyancy of the uniformly-sized spheres makes possible reaction processes in which the body of reactant is stationary and the catalyst moves through the reactant at a controlled rate, or is uniformly suspended therein. A process utilizing catalytic, hollow spheres having a density differing from the liquid media by ±0.1 to 0.5 weight percent is illustrated in FIG. 2. As the catalyst particles 30 are fed from the hopper 34 into the reactor 36, they will deploy to form a uniform suspension 37 within the body 36 of liquid reactant. This reactor can be operated as a batch reactor in which reactants are introduced through inlet 38 and are removed at the end of the run through outlet 40. The catalyst can be separated by means of a screen or filter 42 and recycled to the hopper 34.

Continuous flow processes can be operated by flowing reactant through a bed of catalyst restrained between porous barriers such as screens. The catalyst spheres may tend to pack against the upstream screen unless they are allowed to expand as in a fluidized bed reactor as shown in FIG. 3. The catalyst particles 30 are placed in the reactor 31 downstream of perforated plate 42. The gaseous or liquid reactant is introduced through the inlet 44 placed upstream of the plate. The particles 30 expand by the action of the flowing stream to form a fluidized bed 46. A further screen or perforated plate 48 may be placed towards the top of the reactor to prevent any catalyst particles from being carried out the outlet 50 with the reaction products.

A batch reactor with an autogenously moving catalyst suspension is illustrated in FIG. 4. In this process, the catalyst particles 52 are of uniform size and density and have a density preselected to a value from 0.5 to 10 percent heavier than that of the liquid reactant media 54 within the reactor 56 so that the transit time of the particles within the reactor provides a desired degree of conversion of the reactants. As the catalyst spheres 52 deploy into the reaction media 54 from the hopper 58, they will form a uniform suspension which slowly falls to the bottom of the vessel at a controlled rate. Reactants can be intermittently or continuously fed to the reactor from the inlet 60 and reaction product can be intermittently or continuously removed through outlet 62 containing a liquid-solid separator 64 to remove catalyst particles 52 for recycle to the hopper 58.

FIG. 5 illustrates a batch or continuous process utilizing catalyst particles 70 which are lighter than the reaction media by 0.5 to 10 percent by weight and have a density preselected to provide a desired rate of travel of the particles through the column 72 of reactant. The spherical catalyst particles 70 are fed from a supply vessel 74 into the bottom of the reactor 76 and slowly rise as a suspension through the column 72 of reactant. The catalyst particles can be removed by a skimmer 78 and recycled through line 80 to the supply vessel 74. The reaction product can be recovered through an outlet 82 or by overflow intermittently or continuously. Similarly, reactant material can be introduced through the inlet 84 continuously or intermittently.

In the embodiment shown in FIG. 6, the catalyst suspension and reactant column move continuously under counter-current flow conditions. This process also illustrates use of two different catalysts for a two-stage process. The reactor 80 includes two circulation loops 83, 85. In the first loop 83, a first reactant, R1, is fed into the inlet 86 from the supply tank 88 and pump 90 and forms a rising column 92 of reactant. First stage product can be removed through outlet 94 and recycled through line 96 to the inlet side of the pump 90 when the three-way valve 98 is turned toward the recycle line 100.

First stage catalyst 91 is fed into the inlet 102 of loop 85 from hopper 104, rises through the column 92 of reactant and is removed through outlet 106. The first stage catalyst is recycled through line 108 until the reaction is complete. Valve 110 is turned toward line 112 and all the first stage catalyst is returned to the hopper 104. Valve 114 is opened to feed second stage catalyst 116 into the loop 85 and reaction column 92. Additional reactant, R2, may now be fed from tank 116 into inlet 86 by opening valve 118.

The three-way valve 98 is turned toward recycle. The second stage catalyst is cycled through the column 92 until the reaction is complete. The three-way valve is then turned toward vessel 120 and the second stage reaction product is recovered.

It is to be understood that only preferred embodiments of the invention have been described and that numerous substitutions, modifications, and alterations are permissible without departing from the spirit and scope of the invention as defined in the following claims.

We claim:
1. A heterogeneous catalyst comprising hollow, spherical, gas-impervious particles comprising a metal shell containing a gas at a pressure above atmospheric and having a layer of catalyst on the surface thereof.
2. A catalyst according to claim 1 in which the diameter of the particles is from 0.20 mm to 5.0 mm.
3. A catalyst according to claim 1 in which the catalyst layer includes a metal.
4. A catalyst according to claim 3 in which the metal is selected from transition metals and noble metals and the catalyst includes an activator and/or promoter.
5. A catalyst according to claim 1 in which the gas is air.

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