Catalytic, Hollow, Refractory Spheres, Conversions With Them

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Improved, heterogeneous, refractory catalysts are in the form of gas-impervious, hollow, thin-walled spheres (10) suitable formed of a shell (12) of refractory such as alumina having a cavity (14) containing a gas at a pressure greater than atmospheric pressure. The wall material may be itself catalytic or a catalytically active material 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.
CATALYTIC, HOLLOW, REFRACTORY SPHERES, CONVERSIONS WITH THEM

DESCRIPTION

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).

Cross-Reference to Related Application

This is a division of application Ser. No. 841,062, filed Mar. 18, 1986, now U.S. Pat. No. 4,701,436, which in turn is a continuation-in-part of application Ser. No. 602,901, filed Apr. 23, 1984, now U.S. Pat. No. 4,576,926.

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 or 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, to convert olefins to alkanes, benzene to cyclohexane or nitro groups to amine groups. Transition metal catalysis 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.

Bauer, 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 200°–700° C. Pilch, et al. [U.S. Pat. No. 3,538,018] disclose an improvement over Bauer, et al., in which compact catalyst particles are added to the hollow spheres to form a mixture having a controlled density. A0 [U.S. Pat. No. 3,798,176] manufactures controlled-density, catalyst pellets having a vacant or a dense center. A0 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 pelleting 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 catalytic 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 fluid reaction medium or can flow through the body of fluid reaction medium 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 thickness 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 produced 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 spheres. The catalysts 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 heterogeneous reactions such as hydrocarbonation, polymerization or oligomerization, isomerization, etc.

These and many other features and attendant advantages of the invention will become apparent as the invention is considered in conjunction 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 containing 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 reactor with continuous circulation of catalyst and continuous 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 having a gas-impermeable hollow interior cavity contains a gas such as air under pressure. The pressure of the gas and the thickness and weight of the shell and any promoter or initiator layers thereon are selected to provide a pre-determined density in relation to the density of the fluid reaction media. The shell may be formed of a catalytically active metal such as platinum or aluminum or a noncatalytically active refractory support such as alumina on which is coated a layer of catalyst, e.g., platinum or iron. The catalyst layer may be from 0.1 μm to 0.1 mm in thickness. The catalyst layer may contain from 1 to 25 percent by weight of a promoter, or the initiator may be coated onto the surface of the catalyst layer. The layers, may be formed by deposition of the compounds from the vapor or liquid phase such as by thermal decomposition of metal carbonyls and the like.

Refractory materials that withstand high temperature of 2000° F. to 5000° F. or more without melting or decomposing fluid use in high temperature catalytic reactions. The refractory material can be a metal or alloy such as tungsten or a metal compound such as an oxide, nitride, carbide, boride or silicide, silicate, aluminate or mixtures thereof. The oxide can be a magnesia, beryllia, silica or alumina or mixtures thereof. The hollow, refractory catalytic sphere may have inherent catalytic properties or can be modified to have catalytic properties by adding 0.1 to 25 percent by weight of a catalytic metal such as cobalt, molybdenum, nickel, chromium, iron, copper, tungsten, silver, tin, vanadium, platinum or palladium to the refractory shell or by coating the metal onto the surface of the refractory sphere. Catalysts, particularly useful as oxidizing catalysts for treating automobile exhaust are formed by coating platinum onto alumina or aluminosilicate spheres.

Gas-filled, spherical, metal or refractory shells, that are dimensionally precise, smooth and of high strength can be produced by a method based on the hydrodynamic instability 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 dynamic instability of an annular jet of molten metal as disclosed in U.S. Pat. No. 4,344,787.

The oscillation growth is so rapid that the nonlinear oscillations are dimensionally precise, smooth and of high strength can be produced by a method based on the hydrodynamic instability 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 dynamic instability of an annular jet of molten metal as disclosed in U.S. Pat. No. 4,344,787.

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with the physical process of shell formation, the diameter of the product will be approximately twice that of the jet orifice, whereas the relative wall thickness is not so simply determined. That quantity is not only a function of the aspect ratio of the annular passageway, but is simultaneously a function of the volume flow rate of the fill gas. An increase in the gas flow rate at fixed liquid rate results in an increase in the bubble formation frequency and in a concomitant decrease in wall thickness.

Tin and aluminum shells ranging in diameter from 750–2000 μm and wall thicknesses of about 25 μm have been formed in quantity. Here, the metal jet issued into ambient air. Examination of specimens was made by means of scanning electron micrography (SEM). For shells at the upper size limit, it was found that the spherical specimens were spherical to within about one percent except near two diametrically opposing points from which the jet pinchoff had occurred.

Metallic shells have been produced by the jet instability method at rates up to a few thousand per second. The shells exhibit excellent uniformity in size, good sphericity over most of the surface and fair concentricity. The spheres have excellent surface quality and high tensile strength. The shells are then further coated with catalyst and promoter layers. As a specific example of practice, aluminum spheres about 2 mm in diameter, with a wall thickness of about 25 μm and an internal air 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 produce gas containing CH₄, C₂H₆, C₃H₈, C₅H₁₀, other alkanes, olefins, alcohols, aldehydes and acids.

The ability to adjust the buoyancy of the uniformly-sized spheres make possible reaction processes in which the body of reaction medium is stationary and the catalyst moves through the reaction medium at a controlled rate, or is uniformly suspended therein. A process utilizing catalytic, hollow spheres 30 having a density differing from the liquid medium 32 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 reaction medium. 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 may be operated by flowing reaction medium 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 phase 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 of the outlet 50 with the reaction products.

A batch reactor with an autogeneously 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 reaction media 54 within the reactor 56 so that the transmit 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 reaction medium. The catalyst particles can be removed by a skimmer 78 and recycled through line 80 up 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 reaction column move continuously under counter-current flow conditions. This process also illustrates use of two different catalysts for a two-stage process. The reactor 86 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 reaction medium. 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 reaction medium 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 valves 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 reaction medium media comprising a liquid reactant containing a suspension of hollow, gas impervious catalyst spheres formed of a refractory compound shell having a catalytic active surface and containing a gas at a pressure greater than atmospheric, said spheres having a preselected density in the range of +10 percent of the density of the liquid reaction medium.

2. A reaction media according to claim 1 in which the spheres have a density within +0.5 percent of the density of the liquid reaction medium and form a uniform stationary suspension therein.

3. A reaction medium according to claim 1 in which the spheres have a density less than the density of the liquid reaction medium by 0.5 to 10 percent and form a suspension that slowly rises therethrough.

4. A reaction medium according to claim 1 in which the spheres have a density greater than the density of the fluid reaction medium by 0.5 to 10 percent and form a suspension that slowly falls therethrough.

5. A reaction medium according to claim 1 in which the diameter of the sphere is from 0.20 mm to 5.0 mm.

6. A reaction medium according to claim 5 in which the shell of the sphere consists essentially of an oxide, nitride, carbide, silicide, boride, silicate, aluminate or a mixture thereof.

7. A reaction medium according to claim 1 in which the catalytically active surface comprises a catalyst layer deposited on the shell.

8. A reaction medium according to claim 1 in which the catalytically active surface is formed by catalytically active materials present in the shell.

9. A reaction medium according to claim 7 in which the catalyst layer includes a catalytically active metal.

10. A reaction medium according to claim 9 in which the catalytically active metal is selected from transition metals and noble metals and the catalyst layer includes an activator and/or promotor.

11. A reaction medium according to claim 1 in which the gas is air.

12. A reaction medium according to claim 1 in which the density of the spheres does not vary more than +0.5 percent by weight.

13. A method of catalytically converting a reactant into a product comprising the steps of:
   forming a uniform suspension of hollow, gas-impervious catalytic refractory compound spheres within a body of;
   catalytically reacting the reactant to form a reaction product; and
   separating the catalyst spheres from the reaction product.

14. A method according to claim 13 in which the spheres have a uniform diameter and a preselected density within +10 percent of the density of the fluid liquid reaction medium.

15. A method according to claim 14 in which the spheres have a density within +0.5 percent of the density of the fluid liquid reaction medium and form a uniform stationary suspension therein.

16. A method according to claim 14 in which the spheres have a density less than the density of the fluid liquid reaction medium by 0.5 to 10 percent and form a suspension that slowly rises therethrough.

17. A method according to claim 14 in which the spheres have a density greater than the density of the fluid liquid reaction medium by 0.5 to 10 percent and form a suspension that slowly falls therethrough.

18. A method according to claim 13 in which the diameter of the spheres is from 0.20 mm to 5.0 mm.

19. A method according to claim 13 in which the refractory compound is selected from oxides, nitrides, carbides, silicides, borides, silicates, aluminates or mixtures thereof.