Abstract

The improved, heterogeneous catalysts are in the form of gas-impervious, 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.

12 Claims, 2 Drawing Sheets
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).

This a division 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-impermeable, catalytic spheres having a preselected 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 poisoning 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 or 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 catalysts also show activity for a wide variety of industrially important reactions such as isomerization, hydroformylation, carboxylation, 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 produced 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 mi-
motors 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 prior heterogeneous reactions such as hydrogenation, polymerization or oligomerization, isomerization, etc.

These and many other features and attendant advantages of the invention will become apparent as the invention becomes better understood by reference to the following detailed description when 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 **10** having a gas-impermeable 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 platinum or iron or may be formed of another metal such as aluminum on which is coated a 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 catalyst layer. The layers **16**, **18** 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.

Gas-filled, spherical, metal 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 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 circular 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 axisymmetric oscillations. These culminate in a rapid pinchoff of the jet and in the formation of liquid shells which can be described as thick-wall bubbles. A remarkable feature of the instability is that it is more powerful by far than the familiar Rayleigh instability of a nonhollow jet.

The oscillation growth is so rapid that the nonlinear motion regime is attained within three or four jet diameters, and pinchoff ensures quickly. The motion is highly deterministic; although the action occurs spontaneously and without external stimulus, a frequency stability and corresponding uniformity in shell mass exceeding one part in 10⁴ is readily attained. As each shell in turn parts from its neighbors, it undergoes a ringing oscillation which has the beneficial effect of promoting a centering of captured gas.

The dimensions of shells produced by nozzles of this type may be varied over wide limits. In accordance 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 specimens were spherical to within about one percent except near two diametrically opposing points from which the jet pinchoff had occurred.

Metallurgical 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 shells 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 \( \mu \)m and an internal air pressure of about 100 psi could be coated with a 0.1 \( \mu \)m 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 \( N_2 \) and \( H_2 \) gases at 400° C. and several hundred atmospheres of pressure. Further coating the iron layer with a layer of \( Na_2O \) or \( K_2O \) results in a synthesis gas conversion catalyst which converts \( CO \) and \( H_2 \) gases into product gas containing \( CH_4, C_2H_6, C_3H_8, C_7H_10, \) 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 reactant is stationary and the catalyst moves through the reactor at a controlled rate, or is uniformly suspended therein. A process utilizing catalytic, hollow spheres having a density differing from the liquid media by \( \pm 0.1 \) to 0.5 weight percent is illustrated in FIG. 2. As the catalyst particles are fed from the hopper into the reactor, they will deploy to form a uniform suspension therein. This reactor can be operated as a batch reactor in which reactants are introduced through inlet and are removed at the end of the run through outlet. The catalyst can be separated by means of a screen or filter and recycled to the hopper.

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 a fluidized bed reactor as shown in FIG. 3. The catalyst particles are placed in the reactor downstream of perforated plate. The gaseous or liquid fluid reactant is introduced through the inlet placed upstream of the plate. The particles expand by the action of the flowing stream to form a fluidized bed. A further screen or perforated plate may be placed towards the top of the reactor to prevent any catalyst particles from being carried out of the reactor with the reaction products.

A batch reactor with an autogenously moving catalytic suspension is illustrated in FIG. 4. In this process, the catalyst particles 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 within the reactor so that the transit time of the particles within the reactor provides a desired degree of conversion of the reactants. As the catalyst spheres deploy into the reaction media from the hopper, 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 and reaction product can be intermittently or continuously removed through outlet containing a gas at a pressure greater than atmospheric and having a layer of catalyst on the surface thereof, said spheres having a preselected density not varying more than \( \pm 10 \) percent of the density of the fluid reactant.

A reaction medium according to claim 1 in which the spheres have a density within \( \pm 0.5 \) percent of the density of the fluid reactant and form a uniform stationary suspension therein.

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

In a method of catalytically converting a fluid reactant into a product, the improvement comprising the steps of:

1. A reaction medium comprising a fluid reactant containing a uniform suspension of uniformly-sized, hollow, gas-impermeable catalyst spheres in the form of a gas-impermeable shell containing a gas at a pressure greater than atmospheric and having a layer of catalyst on the surface thereof, said spheres having a preselected density not varying more than \( \pm 10 \) percent of the density of the fluid reactant.

2. A reaction medium according to claim 1 in which the spheres have a density within \( \pm 0.5 \) percent of the density of the fluid reactant and form a uniform stationary suspension therein.

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

5. In a method of catalytically converting a fluid reactant into a product, the improvement comprising the steps of:

   forming a uniform suspension of uniformly sized, hollow, gas-impermeable catalytic spheres within a body of the fluid reactant, said spheres being in the form of a gas-impermeable shell containing a gas at a pressure above atmospheric, having a layer of cata-
7. A method according to claim 5 in which the catalyst layer includes a transition metal or noble metal catalyst and the catalyst further includes an activator or promoter.

8. A method according to claim 5 in which the density within ±10 percent of the density of the fluid reactant; catalytically reacting the reactant by means of the catalyst spheres from the reaction product; catalytically reacting the reactant by means of the catalyst spheres from the reaction product; and separating the catalyst spheres from the reaction product.

9. A method according to claim 5 in which the diameter of the spheres is from 0.20 mm to 5.0 mm.

10. A method according to claim 9 in which the density of the fluid reactant and form a uniform stationary suspension therein.

11. A method according to claim 9 in which the promoter.

12. A method according to claim 11 in which the slowy rises therethrough.

13. A method according to claim 11 in which the slowy rises therethrough.

14. A method according to claim 11 in which the slowy rises therethrough.

15. A method according to claim 11 in which the slowy rises therethrough.