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(54) CATALYST SYSTEM

(71) We, ENGELHARD MINERALS & CHEMICALS CORPORATION, of 70 Wood Avenue South, Metro Park, Plaza, Iselin, New Jersey, United States of America, a corporation organized under the laws of the State of Delaware, one of the United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates generally to catalyst systems and more particularly to catalyst configurations for catalyst systems which operate at high temperatures.

Catalyst systems are designed to operate within a prescribed operating temperature range. If the prescribed temperature range is exceeded, the catalyst activity may be destroyed or otherwise rendered ineffective. In particular, if a low ignition temperature is to be maintained at the front end or upstream portion of the catalyst, the catalytic activity at the front end is to be maintained at a substantially constant level.

In most present catalyst systems which operate essentially adiabatically, the normal operating temperature of the downstream portion of the system (the hottest part of the system) may be as high as about 815°C or slightly higher, and catalyst compositions are available which provide both satisfactorily high activity and temperature stability at this temperature. Only the downstream portion approaches the highest temperatures because, during the steady state operation of an essentially adiabatic catalyst system supporting a typical exothermic reaction, a temperature distribution is established along the length of the catalyst, the downstream portion of the catalyst being at the highest temperature and the initial or upstream portion of the catalyst being at a lower temperature.

In combustion systems utilizing a catalyst, for example, of the kind disclosed in U.S. Patent Specification No. 3,928,961, operating temperatures on the order of about 950°-1750°C are not uncommon at the downstream portion of the catalyst. Such systems therefore utilize a catalyst composition which retains substantial catalyst activity at high temperatures. The system, however, must maintain a low ignition temperature to be effective despite the fact that such catalyst compositions are relatively less active than catalysts operating at lower temperatures.

Honeycomb catalyst systems such as that described in U.S. Patent Specification No. 3,928,961, may be operated so that the temperature of the upstream portion of the catalyst configuration is determined primarily by heat transfer by both thermal conduction and radiation, from the downstream portion of the catalyst. In honeycomb catalysts in particular, heat transfer due to radiation may be substantial because of line of sight paths from the downstream portion to the upstream portion. The temperature of the upstream portion under steady state conditions can be accurately estimated in accordance with the accepted principles of heat transfer by taking into account (1) the rate of heat transfer due to thermal conduction from the downstream portion to the upstream or initial portion of the catalyst system and (2) the rate of heat transfer due to radiant heat transfer from the downstream portion of the catalyst system to the upstream portion. The rate of heat transfer due to thermal conduction is proportional to the temperature difference between the upstream and downstream portions, while the rate of heat transfer due to radiation is proportional to the difference between the downstream temperature raised to the fourth power and the upstream temperature-

ture raised to the fourth power. Thus, when the downstream temperature is very high, the temperature at the initial portion is determined primarily by radiant heat transfer, and as a result, the temperature of the initial portion of the catalyst system is higher than would be predicted by thermal conduction alone.

The very high temperatures at the downstream end of a honeycomb catalyst may be important and critical because the correspondingly higher temperatures at the initial portion may restrict the use of highly active catalyst compositions at the initial portion of the catalyst system. This may be a serious problem if an active catalyst is used to advantageously provide the system with a relatively low ignition temperature. Thus, in order to maintain a low ignition temperature, catalyst activity is to be maintained. However, high temperatures at the initial portion maintained under steady state conditions may tend to deactivate the catalyst composition at the initial portion of the catalyst system, thereby causing an undesirable rise in the ignition temperature of the system for subsequent start-up.

One deactivation mechanism is a loss of base surface area, for example due to sintering of the base composition. The surface area of the base can be measured by the well known method developed by Brunauer, Emmett and Teller. Another deactivation mechanism would be the growth of metal crystallites and the corresponding loss of active metal surface area. The size of the crystallites can be measured by chemisorption, for example by measuring the amount of H_2 or CO which is adsorbed under specified test conditions. The above test methods can also be used to provide measurements to correlate with the catalytic activity of the catalyst.

According to the present invention there is provided a system for catalyzing exothermic reactions comprising (a) a casing having an upstream and a downstream portion and upstream and downstream ports for passage of reactants or hot exhaust gases containing reactable components through the portions and (b) at least one catalytic unit for use within the downstream portion and at least one catalytic unit for use within the upstream portion, the units being mounted in sequence within the casing between said upstream and downstream ports, said catalytic units comprising honeycomb-type catalytic structures of differing efficiency and thermal stability and having an area and pore structure sufficient to permit passage of exhaust or reactant gases through each unit under normal operating conditions, the upstream and downstream portions having respec-

tively first and second longitudinal axes and the honeycomb structure of the less thermally-stable catalytic unit or units, in sequence, being protected from that of the more thermally-stable catalytic unit or units within the casing by the fact that (a) said first and second longitudinal axes are out of alignment with each other so that the heating effect of direct line-of-sight radiation from hotter running catalytic unit(s) to catalytic unit(s) designed for cooler operating temperatures is prevented or reduced, and by the fact that (b) the former unit or units are physically separated from the latter unit or units to reduce heat conduction therebetween thereby permitting greater flexibility in the choice of more efficient cooler running catalysts.

The invention also provides a method of effecting a catalytically-supported thermal combustion of an air-fuel mixture, the fuel being in vaporous form and being intimately admixed with the air, which method comprises contacting the mixture with a catalyst system of the invention to effect combustion under substantially adiabatic conditions.

The catalyst system of the invention is usually capable, at its downstream portion, of operating at temperatures above about $815^\circ C$ while maintaining at the upstream portion of the system, a substantially constant low ignition temperature by preventing thermal conduction and radiant heat transfer from the downstream portion of the catalyst system to the upstream portion. The system usually ensures greater reliability for repeated ignition of the system at low inlet temperatures and usually enables lower ignition temperatures to be obtained by the use of a more active but less temperature stable catalyst composition at the initial portion of the catalyst system.

In a particular embodiment, the upstream portion is more catalytically active than the downstream portion and need not retain its catalytic activity at high temperatures as required by the downstream portion. An example of a catalyst which tends to lose its catalytic activity at high temperatures is crystalline aluminosilicate. The reduction in radiant heat transfer from the downstream to the upstream portion is effected by configurations which tend to eliminate or reduce line of sight radiation paths from the downstream portion to the protected upstream portion. The configurations often include apparatus coated with a high reflectivity surface in order to enhance the radiation reducing character of the configuration.

For a better understanding of the invention, reference will now be made, by way

of example, to the accompanying drawings in which:

Figure 1 is a schematic representation of an unprotected catalyst system; and

5 Figures 2 and 3 are schematic representations of particular embodiments of a protected catalyst system according to the invention.

Referring to Figure 1, there is shown in 10 schematic representation a honeycomb catalyst system 10 of the type described in the above mentioned U.S. Patent Specification No. 3,928,961. The catalyst system may be conceptually divided into three 15 zones which correspond to the classes of mechanisms which control the reaction (combustion) rate at the various points along the catalyst length. For simplicity, Figure 1 shows these zones as being distinctly defined, however in reality, the 20 boundaries between the zones are diffuse, and in addition the proportions of the zones are exaggerated for illustrative purposes.

25 While the mechanism of honeycomb catalyst operation forms no part of the present invention, it is believed that the catalyst system of Figure 1 operates as follows: When the honeycomb catalyst 30 system 10 is presented with a fuel/air mixture at a temperature only slightly above the ignition temperature of the particular catalyst composition being used, the reaction rate in an initial portion 12 of the 35 catalyst system will be slow, and will be controlled by intrinsic catalytic kinetics. In the initial portion 12, differences in temperature and species concentration between the honeycomb catalyst walls and 40 the bulk fluid flowing through the honeycomb channels are relatively small. In particular, for an exothermic reaction such as combustion, the wall temperature is equal to or only moderately greater than the bulk 45 fluid temperature.

As the gas passes through the initial portion of catalytic system 10 operating at steady state, the bulk fluid temperature increases due to absorption of the heat of 50 reaction. Since the intrinsic chemical reaction rate increases exponentially with temperature, this rate soon exceeds the rate at which the reactants can be transported to the honeycomb catalyst walls and under 55 this circumstance, the reaction becomes controlled by the rate at which the reactants are convectively or diffusively transferred to the surface of the catalyst. This occurs in a second portion 14 of the 60 catalyst system, where the rate of mass-transfer to the catalyst wall surface determines the overall reaction rate. (If the inlet temperature of the fuel/air mixture is sufficiently high, the initial portion may not 65 exist at all, and the "second portion" will

be the first zone in the catalyst system). In the second portion, the temperature of the honeycomb catalyst wall can greatly exceed the bulk of fluid temperature and in fact can approximate the adiabatic flame temperature of the inlet fuel/air mixture. 70

As the bulk gas temperature increases further in passing through the second portion 14, a temperature will eventually be 75 reached where the rate of the homogeneous or thermal combustion reaction becomes significant. For methane fuel, for example, this temperature corresponds to about 1000°C. Beyond this approximate 80 temperature, within the catalyst, the heterogeneous and homogeneous reactions proceed simultaneously. This occurs in a third portion 16 of the catalyst system. In the 85 third portion, the catalyst wall temperature continues to approximate the adiabatic flame temperature, while the gas temperature in the interior of the honeycomb catalyst passageways becomes increasingly high until it also may approach the adiabatic 90 flame temperature.

In a typical catalyst system, operating as described above, the catalyst temperature in the initial portion 12, while initially relatively low and approximately equal to 95 the temperature of the incoming air/fuel mixture, will, as the catalyst system reaches a steady state condition, increase and tend to approach the temperature of the downstream portions of the catalyst. The phenomenon results, as noted above, from thermal 100 conductions along the catalyst and catalyst support walls and from radiant heat transfer from the hotter downstream portions of the catalyst to the upstream portions. Thus, initial zone 12 tends to reach 105 a relatively high temperature during steady state operation of the catalytic combustor system.

Referring to Figures 2 and 3, there are shown particular embodiments of the invention in which an upstream portion 20 110 of the catalyst system is protected from the hotter downstream portion 26 of the catalyst system. Protected upstream portion 20 will include all or a part of initial portion 115 12 and may also include a part of second portion 14. (If there is no initial portion 12, protected upstream portion 200 will include only a part of second portion 14). Protection against thermal conduction is 120 achieved by physically separating the protected upstream portion 20 of a catalyst system from the downstream portion of the catalyst system. As shown in Figures 2 and 3, each of the upstream and downstream 125 portions of the catalyst system will be seen to have an upstream face (to the left of the respective portions as seen in the drawings) and a downstream face (seen to the right in the drawings). The aforementioned 130

physical separation or spacing apart, as referred to hereinbelow with respect to Figures 2 and 3, may be effected by securing the upstream and downstream portions of the catalyst system so as to be substantially free of continuous thermal conduction paths through solid material between the upstream face of the downstream portion and the downstream face of the upstream portion. Protection against radiant heat transfer from the downstream portion of the catalyst system to the protected upstream portion is achieved by virtue of the fact that the axes of the upstream and downstream portions are out of alignment with each other to prevent or reduce the heating effect of line of sight radiation from the downstream portion to the upstream portion. In this way, not only is the upstream portion of the catalyst protected against excessive temperatures but unique advantages are realized, the ability to construct the two portions of the catalyst system from different catalyst compositions and/or from different catalyst substrates in order to maintain a low ignition temperature and to maximize the efficiency and operation of the catalyst system at maximum cost.

Figure 2 shows a catalyst system in which the longitudinal axis of the protected upstream portion is oriented 180° away from (or in the opposite direction from) the longitudinal axis of the downstream portion. In addition to the reduction in heat transfer between the portions 20 and 26 resulting from the physical separation of portions 20, 26, thermal conduction and radiant heat transfer are further reduced by using an enclosing wall 50 having low reflectivity, low conductivity properties and forming part of the casing between the portions 20 and 26. Referring to Figure 3, the longitudinal axes of the upstream and downstream portions 20, 26 are perpendicular to one another. This physical configuration reduces radiant heat transfer and thermal conductivity between the two portions 20, 26 of the catalyst system. Additionally, the temperature of the protected upstream portion 20 is preferably further reduced by using an enclosing wall 52 having low reflectivity and low thermal conductivity properties and forming part of the casing between portions 20 and 26. In this way a low ignition temperature can be maintained at the protected upstream portion.

Separating the catalyst system into the upstream and downstream portions offers several distinct advantages. For example, it enables the use of different catalyst compositions in each of the catalyst portions; this is particularly advantageous at the protected upstream portion where a low

ignition temperature is desirable. Also, a less expensive catalyst composition can be used in the higher temperature downstream portion. For example highly-active but thermally-less-stable catalyst composition can be used in the protected upstream portion while a less active catalyst composition is used downstream. Thus, according to the invention, mordenite and other molecular sieves, which lose their surface area at 850 and 1000°C, but which are highly desirable supports for very active catalysts at temperatures lower than their thermal decomposition temperatures, can be used in the protected upstream portion of a typical catalyst system in which the downstream portion may be operating at, for example, 1500°C. The downstream portion, on the other hand, may require a slip with greater resistance to thermal sintering, such as chromia-alumina-ceria as a base for deposition of an active metal oxidation catalyst. Alternatively, the downstream portion may not require any slip at all, where, for example, an active metal may be deposited directly on a thermally-stable honeycomb by decomposition of an organo metallic compound.

The protected upstream portion 20 of the catalyst systems shown in Figures 2 and 3 can be made, for example, as follows: A zircon-mullite honeycomb cylinder, 1" in diameter by 3" long and having 12 corrugations per inch, is impregnated with a catalytic base consisting of an aqueous suspension of 12% CeO₂-88% Al₂O₃ particles in the 4 micron size range. The coated honeycomb is dried at 110°C and then calcined at 600°C. The surface area of the base is greater than 100 m²/gm. The base content was 22.5% by weight.

The base-coated honeycomb cylinder is then immersed in a 25% Na₂PdCl₄ solution for 15 minutes. The solution is then blown off lightly with air. The honeycomb is then immersed into a slightly basic solution for one hour, rinsed with water and dried at 110°C. The cylinder is then calcined at 500°C.

A second impregnation of the cylinder is made with another 25% solution of Na₂PdCl₄ for 15 minutes. The honeycomb cylinder is then removed from the solution, blown off, and is immersed in a slightly basic medium for one hour. The cylinder is placed in a water bath for 15 minutes and is then washed chloride free and dried at 110°C for 2 hours. On cooling the cylinder is found to contain 2.6 wt.% total palladium.

The downstream portion 26 of the catalyst system shown in Figures 2 and 3 can be constructed, for example, from a 5 corrugation per inch zircon-mullite honeycomb prepared as follows: A refractory

base consisting of $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{CeO}_2$ (14%/70%/16%) is calcined at 1000°C for four hours. It is then ground to forty mesh powder having surface area of 50 sq.m./gm. The powder is then ball milled with palladium nitrate in water, forming a ground aqueous slurry having a 2-3 micron average particle size. The 5 corrugation per inch zircon-mullite honeycomb is dipped in this aqueous slurry blown off with air, dried at 110°C , and is then calcined at 500°C for two hours. The base content of this honeycomb catalyst preparation is 22.7% by weight and the palladium content of the honeycomb is 0.38% by weight.

WHAT WE CLAIM IS:—

1. A system for catalyzing exothermic reactions comprising (a) a casing having an upstream and a downstream portion and upstream and downstream ports for passage of reactants or hot exhaust gases containing reactable components through the portions and (b) at least one catalytic unit for use within the downstream portion and at least one catalytic unit for use within the upstream portion, the units being mounted in sequence with the casing between said upstream and downstream ports, said catalytic units comprising honeycomb-type catalytic structures of differing efficiency and thermal stability and having an area and pore structure sufficient to permit passage of exhaust or reactant gases through each unit under normal operating conditions, the upstream and downstream portions having respectively first and second longitudinal axes and the honeycomb structure of the less thermally-stable catalytic unit or units, in sequence, being protected from that of the more thermally-stable catalytic unit or units within the casing by the fact that (a) said first and second longitudinal axes are out of alignment with each other so that the heating effect of direction line-of-sight radiation from hotter running catalytic unit(s) to catalytic unit(s) designed for cooled operating temperature is prevented or reduced, and by the fact that (b) the former unit or units are physically separated from the latter unit or units to reduce heat conduction therebetween, thereby permitting greater flexibility in the choice of more efficient cooler running catalysts.

2. A system as claimed in claim 1,

wherein the supports for the upstream and downstream portions have upstream and downstream faces, and means are provided to insulate and secure the upstream and downstream portions from the casing or other continuous thermal conduction paths between catalytic units generally operating at different temperatures.

3. A system as claimed in claim 1 or 2, wherein the upstream portion includes a catalyst composition which is more catalytically active and less thermally-stable than the catalyst composition of the downstream portion.

4. A system as claimed in claim 1 or 2, wherein the downstream portion includes a catalyst composition which is more catalytically active and less thermally-stable than the catalytic composition in the upstream portion.

5. A system as claimed in any of claims 1 to 4, wherein the upstream portion is formulated to retain a smaller proportion of its virgin catalytic activity after aging at an elevated reaction temperature that does the downstream portion.

6. A system as claimed in any of claims 1 to 5, including means to cool the upstream portion.

7. A system as claimed in any of claims 1 to 6, wherein said first and second longitudinal axes are substantially perpendicular to one another.

8. A system as claimed in claim 7, including, as a radiant heat transfer reducing means, a wall of low reflectivity and low conductivity forming part of the casing between the upstream and downstream portions.

9. A system as claimed in any of claims 1 to 6, wherein said first and second longitudinal axes are substantially parallel to and displaced from one another.

10. A system as claimed in claim 9, including, as a radiant heat transfer reducing means, a wall of low, reflectivity and low conductivity forming part of the casing between the upstream and downstream portions.

11. A system as claimed in any of claims 1 to 10, wherein the upstream portion includes a crystalline aluminosilicate.

12. A method of effecting a catalytically-supported thermal combustion of an air-fuel mixture, the fuel being in vaporous

- form and being intimately admixed with the air, which method comprises contacting the mixture with a catalyst system as claimed in any of claims 1 to 11 to effect combustion under substantially adiabatic conditions.
13. A catalyst system suitable for effecting combustion and other exothermic reactions, substantially as hereinbefore described with reference to, and as shown in Figure 2 or 3 of the accompanying drawings.
14. A method of effecting a catalytically-

supported thermal combustion of an air-fuel mixture, substantially as hereinbefore described with reference to Figure 2 or 3 of the accompanying drawings.

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