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3,377,156 PROCESS OF REDUCING IRON OXIDE ORES WITH GASES CONTAINING CAR- BON MONOXIDE

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ABSTRACT OF THE DISCLOSURE

The reversion of gases containing carbon monoxide to carbon dioxide and carbon when in contact with catalytic metal surfaces at high temperatures is suppressed or inhibited by providing small concentrations of sulfur or heat-decomposable sulfur compounds in the gases. This invention is especially useful in direct iron ore reduction processes.

This invention relates to the production of metallic iron via reduction of iron ores by contact with reducing gases. In particular, it relates to an improved iron ore reduction process wherein fluidized iron ores are metallized by direct contact with carbon monoxide, mixtures of carbon monoxide and hydrogen, or mixtures of carbon monoxide with other gases which can also contain hydrogen.

It is well known to produce metallic iron by reduction of oxidic iron ores, i.e., ores containing or consisting essentially of oxides of iron, in beds fluidized by ascending gases, at temperatures ranging generally from about 1000° F. up to just below the sintering temperature, i.e., about 1800° F. for most ores. In such processes, several fluidized beds are generally provided, and these are staged as separate reduction zones operated at the same or different elevated temperatures. Generally, the several fluidized beds are housed within a single reactor.

In a typical staged fluidized iron ore reduction process, particulate oxidic iron ores are introduced into the top of a reactor and flowed downwardly from one fluidized bed to the next succeeding bed, and within each bed the state of oxidation of the ore is progressively lowered. Thus, the ore flows from one of a series of staged reduction zones to the next lower succeeding stage. Within each of the several stages, the ore is contacted by upwardly flowing gases, and reduced while concurrently the reducing components of the ascending gas is oxidized. If desired, the partially oxidized gas can be regenerated by removal of oxidized components and reused. In the several stages, the ore is reduced, e.g., from ferric oxide to magnetic oxide of iron (or mixture approximating the composition of such compound), from magnetic oxide of iron to ferrous oxide, and from ferrous oxide to substantially metallic iron. Generally, the metallic iron product ranges from about 85 to about 95 percent, and higher, metallic iron.

Such fluidized iron ore reduction processes most often utilize externally generated synthesis gas, i.e., gaseous mixtures consisting of carbon monoxide and hydrogen, or mixtures of these and other gases, which are injected into the bottom stage of the reactor. Such gaseous mixtures are generally formed from hydrocarbon fuels which are oxidized or burned in a deficiency of oxygen. Often such gaseous mixtures are hydrogen-enriched, e.g., via use of the water-gas shift reforming reaction. Because of the endothermic nature of hydrogen in the iron ore reduction reaction, however, it is generally desirable to employ gaseous mixtures wherein carbon monoxide is employed in relatively high concentration in the process.

Often also, it is desirable to form the reducing gas mix-

tures, in whole or in part, in situ. In accordance with this technique, generally termed direct injection, hydrocarbon fuels are fed directly into a stage of the process wherein metallization is high, e.g., perhaps 85 to about 98 percent, so that the reducing gases are generated internally. Thus, metallic iron is catalytic under certain conditions and the fuel is decomposed in situ to a gaseous mixture of carbon monoxide and hydrogen. The presence of carbon monoxide in the gaseous mixture, whether introduced into or generated in situ within the process, is quite desirable, but its presence often creates difficulties.

Gases which contain carbon monoxide even in relatively low concentrations will, under certain conditions, strongly react in the presence of certain metals, particularly iron. Certain forms of liberated carbon will vigorously and rapidly combine with the iron, e.g., the reactor and auxiliary equipment made of iron, so that a severe form of corrosion, i.e., catastrophic carburization, often results. Moreover, free carbon will be formed. This lessens efficiency. Furthermore, the deposition of carbon, inter alia, by reversion of the carbon monoxide to free carbon, causes plugging and failure of e.g. standard heating equipment, pumps and transfer lines. These problems are most acute when carbon monoxide and mixtures of gases containing carbon monoxide are heated at temperatures ranging from about 800° F. to about 1300° F. In fluidized iron ore reduction processes, it is extremely difficult, if indeed possible, to avoid heating such gases through this temperature range and hence the reversion of carbon monoxide to carbon, or creation of conditions for catastrophic carburization is an acute threat.

Even in processes wherein carbon monoxide-containing gaseous mixtures are desirably heated to higher temperatures, e.g., temperatures ranging from about 1300 to about 1800° F., it is extremely difficult, if possible, to avoid cooling the gas through such temperature range. Thus, it is often desired to regenerate the reducing gases for further use by removal of carbon dioxide and water. But, to do so the gases must be cooled through this temperature range. On the other hand, it is often desired to elevate the temperature of a cool gas through this range. Thus, gas preheating is one method of introducing heat to the process. The carbon monoxide reversion problem, then, has been extremely troublesome and has handicapped the development of both indirect and direct injection techniques for the generation and use of carbon monoxide-containing gaseous mixtures in fluidized iron ore reduction processes.

The solution of these and other difficulties is therefore the primary objective of the present invention. In particular, it is the object of this invention to provide a new and improved process which will make feasible the more general use of carbon monoxide-containing reducing gas mixtures by obviating the problems due to carbon monoxide reversion. More particularly, the objective of this invention is to provide a process which will suppress or inhibit reversion of carbon monoxide. A further and more specific objective is to provide the art with a simplified, new and novel fluidized iron ore reduction process, especially one utilizing a series of staged reduction zones, wherein carbon monoxide reversion is drastically suppressed even at temperatures which normally produce acute carbon reversion. It is yet another object to provide such process which is particularly useful in direct hydrocarbon injection.

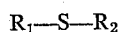
These and other objects are achieved in accordance with the present invention which contemplates the use of small and infinitesimal quantities of sulfur or heat-decomposable sulfur-containing compounds injected, added to, admixed with or otherwise incorporated within the carbon monoxide-containing reducing gas in contact with

catalytic metallic surfaces, especially ferrous metal surfaces, e.g., iron. Such process finds particular application in a fluidized iron ore reduction process. By use of such compounds within the carbon monoxide gas, or gaseous mixture containing carbon monoxide, the gas can be utilized in reducing the iron ore and the reversion of carbon monoxide will be suppressed; and, in some instances virtually eliminated. In particular, it has been found that such gases can be heated or cooled through temperatures ranging from about 800° F. to about 1500° F., and particularly, even from about 900° F. to about 1200° F., even in the presence of metals, but yet carbon monoxide reversion is drastically inhibited or suppressed.

It has been found that as little as one part of sulfur, per million parts of gas can be of some beneficial effect in lessening carbon monoxide reversion in the gaseous reduction mixture. Preferably, however, it is desirable to employ at least about 5 parts to about 1000 parts, and more preferably from about 20 to about 300 parts of sulfur, per million parts of gas, since this concentration effectively suppresses carbon monoxide reversion, and yet does not create significant problems due to acid formation. Under most conditions, optimum benefits are produced by employing from about 50 to about 200 parts sulphur, per million parts of gas. While sulfur concentrations greater than about 1000 parts per million parts of carbon monoxide can be employed, this is not generally desirable inasmuch as, *inter alia*, acid formation increases and there is little, if any, corresponding benefit resulting from the use of the increased sulfur concentration. Significantly higher amounts of sulfur can adversely affect the quality of the resultant metallized product.

The reason for the effectiveness of sulfur or heat-decomposable sulfur-containing compounds in suppressing carbon monoxide reversion is not known. It is believed, however, that the sulfur or sulfur compounds decompose in the process to provide an effective concentration of hydrogen sulfide *in situ* and hence, it is believed that it is in the hydrogen sulfide which actively suppresses carbon monoxide reversion. It is certainly known, however, that hydrogen sulfide is extremely effective, whether added *ab initio* or generated *in situ*, and will suppress carbon monoxide reversion when present in very small concentrations. Therefore, sulfur or any sulfur-bearing compound which will decompose at temperatures below about 1500° F. to form an effective concentration of hydrogen sulfide can be directly employed. On the other hand, sulfur-bearing compounds decomposable at higher temperatures can be indirectly heated to higher temperatures outside the process, or at a specific location within the process, and then injected into the process to suppress carbon monoxide reversion.

Additives particularly suitable for use in accordance with the present invention, whether added to the process *ab initio* or generated *in situ*, are the divalent sulfur compounds, or sulfides. These can be characterized by the following formula



wherein R_1 and R_2 are the same or different and can be hydrogen or monovalent organic radicals, e.g., hydrocarbon radicals, such as alkyl, alkenyl, alkynyl, aryl, arylalkyl, aralkyl and the like. The organo radicals can be substituted or unsubstituted, and where substituted the hydrogen of the radical may be replaced by halogen, nitro groups, amino groups, carbonyl groups and the like; or, the radical, where of ring structure, can be ring substituted to form a heterocyclic radical. The carbon of a ring can be substituted, for example, by sulfur, oxygen, nitrogen, or the like. Preferably, an organo radical should contain no more than about ten carbon atoms, and more preferably about six carbon atoms. Exemplary of these classes of compounds are methyl sulfide, n-propyl sulfide, ethyl n-propyl sulfide, cetyl isoamyl sulfide, bis(trichloromethyl) sulfide, allyl benzyl sulfide, phenyl trichloromethyl sul-

fide, 1-naphthyl phenyl sulfide, 9-methyl mercaptophenanthrene, 3(ethylmercapto) thiophene, 3-ethylcyclohexanethiol, 8-quinolinethiol and the like.

Preferably, the sulfides contain no more than one monovalent organo radical. Exemplary of such compounds are methyl mercaptan, isopropyl mercaptan, n-amyl mercaptan, allyl mercaptan, 3-acridinemercaptan, α -methyl benzyl mercaptan, 2-naphthalene thiol and the like. Mixtures of any of such compounds with other substances or with each other are suitable. Certain commercial mixtures and naturally occurring materials can also provide these compounds, or can be added to the process, to generate the desired compounds *in situ*.

Most preferably R_1 and R_2 are both hydrogen, i.e., hydrogen sulfide. Hydrogen sulfide is an outstanding compound because of its availability, its readily usable form, and its extremely high effectiveness in minute concentrations.

More complex sulfur compounds can also be employed. Other divalent sulfur compounds are thus suitable. These include such compounds as the polysulfides, especially the disulfides illustrative of which are carbon disulfide, methylethyl disulfide, 2-fenchanyl methyl disulfide, tert-butyl-2-naphthyl disulfide, 2-(o-nitrophenyldithio)benzothiazole, and the like.

In a particularly preferred embodiment according to this invention, oxidic ores, as particulate solids particles, are contacted and fluidized with upwardly flowing carbon monoxide-containing gases in a process wherein a plurality of staged zones are provided. The zones which contain the fluidized beds of ore at different stages of reduction can be operated at the same or at different elevated temperatures. Preferably, also, there is provided in accordance with such embodiment, one or more ferric reduction zones operated at temperatures ranging from about 1000° F. to about 1800° F. and one or more, and preferably a plurality, of ferrous reduction zones operated at temperatures ranging from about 1300° F. to about 1700° F. The sulfur or sulfur-containing compound, or compounds, is preferably added to the carbon monoxide-containing reducing gas and then heated prior to or at the time of the injection into the process. Preferably, the carbon monoxide-containing reducing gases within which is provided the sulfur or sulfur-containing compound is injected into a ferrous reduction zone wherein the metallization ranges from about 85 percent to about 98 percent, and higher.

The following nonlimiting examples and pertinent demonstrations bring out the more salient features and provide a better understanding of the invention.

A large quantity of raw hematite ore, i.e. a Carol Lake ore, is pulverized in a ball mill, to a particle size ranging from about 75 to 210 microns, and divided into several like portions.

Example 1

A portion of the ore is charged into a fluidized iron ore reactor or reduction process wherein is provided a series of four staged fluidized zones, two ferric reduction zones and two ferrous reduction zones. The ore is fluidized by an upwardly flowing gas initially of 20 percent carbon monoxide, 60 percent hydrogen, and 20 percent nitrogen to which is added 80 parts of hydrogen sulfide, per million parts of gas. The gas is preheated through a temperature range of 850° F. to 1300° F. and then injected into the lowermost ferrous reduction zone from whence it flows from a zone containing an iron ore at a lower level of oxidation to the next higher level of oxidation, i.e., from the bottom to the top of the reactor. In the top ferric zone the partially oxidized gas is burned with air to provide heat to the various reduction stages and the reduced ore moves from the top to the bottom of the reactor from one stage of reduction to the next. The ferric reduction stages, wherein ferric oxides are reduced essentially to magnetic oxides of iron, are operated at 1300° F. as were the ferrous reduction stages wherein the ferrous

oxide is reduced, in the final stage, to provide 94 percent metallization.

Pursuant to operating at such conditions, the process does not show any significant sign of carbon monoxide reversion even after many hours of continuous operation. There is no indication whatsoever of catastrophic carburetization.

Example 2

The foregoing demonstration is repeated in precise detail employing a second portion of the ore except in this instance 150 parts of hydrogen sulfide, based on the volume of the gas, is added to the entering gas charged into the ferrous reduction zone. The beds appear normal and the process functions normally in every way and there is no evidence of any significant amount of carbon monoxide reversion. The ferrous metal parts of the equipment are not carburized and little carbon is formed in the reaction.

Example 3

When Example 2 is repeated with another portion of ore heated to a temperature of 1400° F. and ethyl mercaptan in concentrations of 200 parts, per million parts of carbon monoxide, is added to the reducing gas mixture, there is yet no significant evidence of carbon monoxide reversion.

Example 4

When the conditions of operation of the process of Example 2 are repeated except that 200 parts of benzyl mercaptan is injected into the process, there is little evidence of carbon monoxide reversion.

When ethyl sulfide, phenyl sulfide, and ethyl propyl sulfide, respectively, are successively added to the process in 100, 150, and 200 parts significant benefits also result. The tendency of carbon monoxide to revert is effectively suppressed.

It has been concluded and firmly established that the sulfur compounds of this invention must be gasified and thoroughly dispersed within the reducing gases at the time of reduction to provide benefits, whether added ab initio or generated in situ from an added material capable of producing such compounds.

It is apparent that certain modifications and changes can be made in the present process without departing the spirit and scope of the invention. The key and novel feature of the invention is the use of small and minor portions of sulfur or heat-decomposable sulfur compounds directly added to, injected within, or otherwise physically dispersed with the reducing gases at the time of use or injection into the fluidized iron ore process.

Such compounds in contact with the gas at the time of contact with catalytic metallic surfaces, or iron, provide benefits, whether added ab initio or generated in situ, from an added material itself capable of providing such compounds.

Having described the invention, what is claimed is:

1. In a process for the production of metallic iron from oxidic iron ores wherein iron ore in particulate form is fed into the process and reduced by a stream of carbon monoxide-containing gas heated to a temperature ranging from above about 1000° F. to just below the sintering temperature of the ore, the improvement comprising heating said reducing gas to said temperature, and adding to said gas an additive selected from the group consisting of sulfur and heat-decomposable sulfur compounds to cause said additive to be present in the gas during the heating thereof, and while the gas is passing through a temperature ranging from about 800° F. to about 1500° F. to suppress reversion of the carbon monoxide.

2. The process of claim 1 wherein the additive is provided in the gas in effective concentration ranging from about 5 to about 1000 parts, per million parts of gas.

3. In a process for the production of metallic iron from

oxidic iron ores wherein iron ore in particulate form is fed into the process, staged in a series of beds fluidized by injecting carbon monoxide-containing gas heated to a temperature ranging from above about 1000° F. to just below the sintering temperature of the ore, and reduced, at least a portion of the reducing gas is oxidized, withdrawn from the process, cooled and regenerated by removal of oxidized components, reheated in the presence of catalytic metal surfaces and thence recycled to the process, the improvement comprising

heating said reducing gas to said temperature, and adding to said gas an additive selected from the group consisting of sulfur and heat-decomposable sulfur compounds to cause said additive to be present in the gas during the heating thereof, while in contact with the catalytic metal surfaces, and while the gas is passing through a temperature ranging from about 800° F. to about 1500° F. to suppress reversion of the carbon monoxide.

4. In a process for the production of metallic iron wherein oxidic iron ore is successively reduced in a plurality of staged fluidized reduction zones with carbon monoxide-containing gases at temperatures above about 800° F., whereby said gases are partially oxidized to carbon dioxide and wherein said partially oxidized gases are cooled below about 800° F. and regenerated for further use and then reheated in contact with catalytic metal surfaces to temperatures above about 800° F., the improvement comprising adding to said regenerated gas before reheating an additive selected from the group consisting of sulfur and heat-decomposable sulfur compounds in an amount sufficient to suppress reversion of the carbon monoxide.

5. The process of claim 4 wherein the additive is hydrogen sulfide in an amount sufficient to provide a concentration of about 5 to about 1000 parts, per million parts of regenerated gas.

6. The process of claim 3 wherein the additive is provided in effective concentration ranging from about 5 to about 1000 parts, per million parts of gas.

7. The process of claim 3 wherein the additive is a divalent sulfur compound provided in effective quantities ranging from about 20 to about 300 parts, per million parts of gas.

8. The process of claim 3 wherein the additive is hydrogen sulfide.

9. The process of claim 3 wherein the additive is provided in effective concentration ranging from about 50 to about 200 parts, per million parts of gas.

10. The process of claim 9 wherein the additive is a divalent sulfur-containing compound.

11. In a process for the production of metallic iron by direct reduction of particulate oxidic iron ores wherein ore is successively reduced in a plurality of staged fluidized reduction zones, including ferric and ferrous reduction zones, operated at temperatures ranging from about 1000° F. to about 1800° F. by preheated carbon monoxide-containing gas injected into a ferrous reduction zone, the improvement comprising adding and maintaining from about 5 to about 1000 parts of an additive selected from the group consisting of sulfur and heat-decomposable sulfur compounds to the gas, based on a million parts of gas, while preheating the gas through a temperature range of from about 800° F. to injection temperature, to suppress carbon monoxide reversion.

12. In a process for the production of metallic iron by direct reduction of particulate oxidic iron ores wherein the ore is successively reduced in a plurality of staged fluidized reduction zones including a ferric and a ferrous reduction zone, and wherein hydrocarbon fuel is directly injected into a ferrous reduction zone operated at temperatures ranging from about 1300° F. to about 1700° F. to generate carbon monoxide-containing gases which reduces the ferrous oxide to from about 85 to about 98 percent metallization, at least a portion of the reducing

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gas is oxidized, withdrawn from the process, cooled, re-generated by removal of oxidized components, reheated in the presence of catalytic metal surfaces and thence rein-jected into the process, the improvement comprising add-
ing to the injected gas from about 5 to about 1000 parts of
an additive selected from the group consisting of sulfur
or heat-decomposable sulfur compounds, based on a
million parts of generated gas, to suppress carbon
monoxide reversion.

13. The process of claim 12 wherein the additive is a

14. The process of claim 12 wherein the additive is
hydrogen sulfide.

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15. The process of claim 5 wherein said hydrogen
sulfide is provided in a concentration of about 20 to 300
parts per million parts of regenerated gas.

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