

[54] **THREE-WAY CATALYTIC PROCESS FOR GASEOUS STREAMS**

[75] Inventors: **James S. Ritscher**, Ossining; **Michael R. Sandner**, Chappaqua, both of N.Y.

[73] Assignee: **Union Carbide Corporation**, New York, N.Y.

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Primary Examiner—G. O. Peters

Attorney, Agent, or Firm—Gary L. Wamer

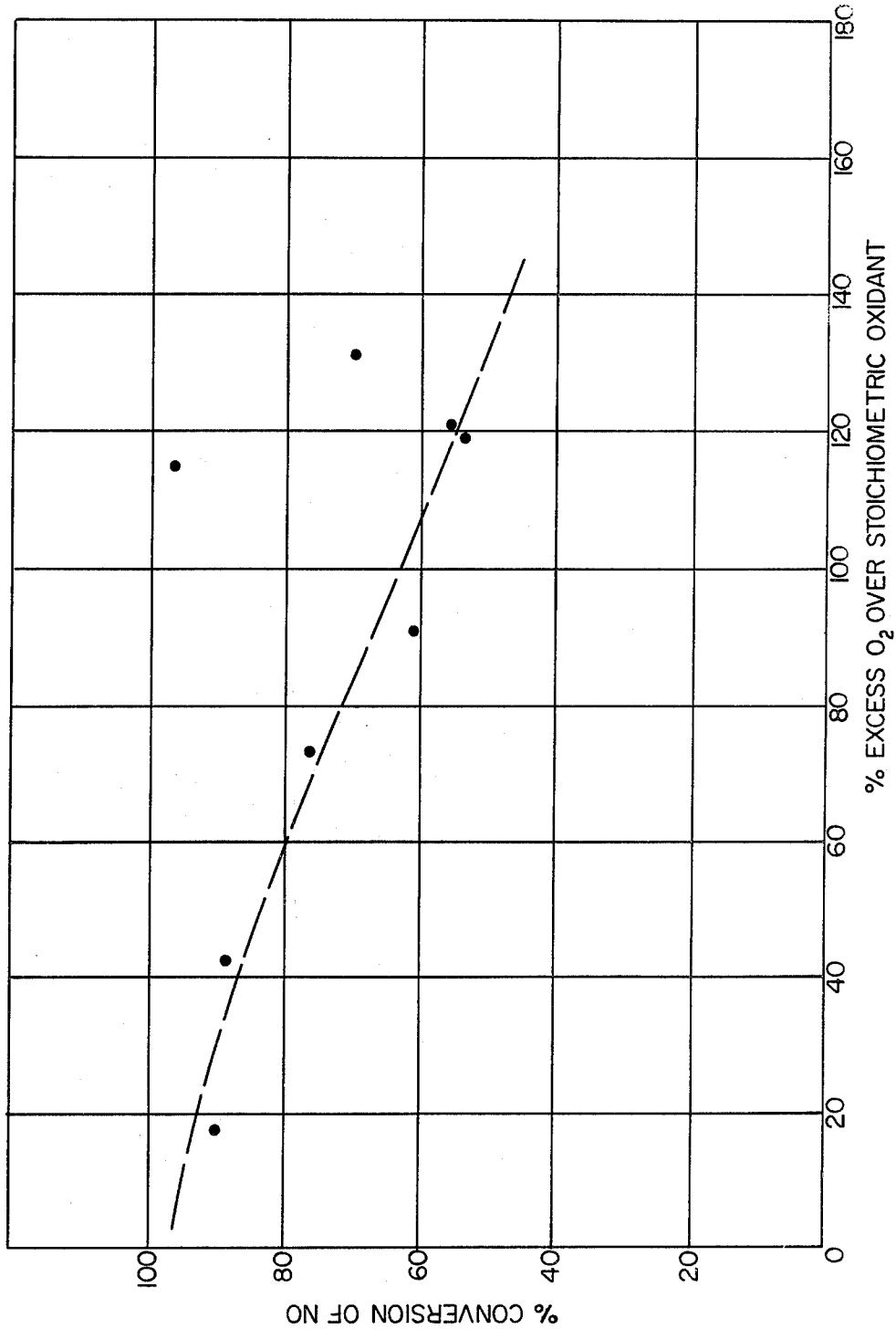
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ABSTRACT

A process for the catalytic combustion of carbon monoxide and hydrocarbons and the catalytic reduction of the oxides of nitrogen contained in a gas stream. The process involves intimately contacting the gaseous stream with a catalyst bed comprising copper metal or copper ion and a high silica zeolite.

12 Claims, 1 Drawing Figure

FIG. 1



THREE-WAY CATALYTIC PROCESS FOR GASEOUS STREAMS

FIELD OF THE INVENTION

This invention relates to a process for the catalytic oxidation of carbon monoxide and hydrocarbons and the reduction of nitrogen oxides contained in a gaseous stream. The process may occur in a stoichiometric excess of oxygen without substantial decrease in the conversion to non-noxious products.

BACKGROUND OF THE INVENTION

One of the most troubling pollution control problems today arises from the emissions of automobiles. The noxious emissions are of essentially three types. These are: (1) carbon monoxide (CO), (2) hydrocarbons (HC) and (3) nitrogen oxides (NO_x).

The simultaneous control of these various pollutants presents a formidable technical problem because of varying nature of the pollutants. Control of carbon monoxide and hydrocarbons is a relatively simple matter to achieve catalytically. The simultaneous control of nitrogen oxides, carbon monoxide and hydrocarbons, by a so-called "three-way" catalyst, is a much more difficult problem.

The need to simultaneously control these three types of pollutants has long been recognized. It has long been known that nitrogen oxides are both pollutants and initiators for complex photochemical reactions with hydrocarbons. The resultant "photochemical smog" is a serious problem. Carbon monoxide is a serious pollutant in and of itself.

Carbon monoxide is a relatively easy pollutant to control and is easily combusted in a catalytic unit to carbon dioxide. Even under an oxygen-deficient atmosphere, carbon monoxide will be combusted to the oxygen limiting value by any noble metal, and many base metal, catalyst.

The catalytic control of various "hydrocarbons" is more difficult. The combustion of hydrocarbons to carbon dioxide and water varies in complexity depending on the nature of the hydrocarbon. The group referred to as "hydrocarbons" includes many different substrates, some being very reactive while others are highly refractory. This group also includes small amounts of hydrogen which is easily oxidized. A small amount of methane is included in this group, and is a hydrocarbon which is relatively difficult to oxidize. Most "hydrocarbon" pollutants are considerably easier to oxidize than methane, but since they only weakly chemisorb on catalytic surfaces, they are more difficult to oxidize than carbon monoxide and hydrogen.

In general the nitrogen oxides troublesome from a pollution standpoint are nitric oxide (NO) and nitrogen dioxide (NO₂) and are both referred to herein by the formula NO_x. The elimination of NO_x is generally achieved by the reduction of NO_x to elemental nitrogen. In theory, NO can be disproportionated to yield N₂ and O₂, since it is thermodynamically unstable with respect to its elements. Even so, there is no known catalyst for this disproportionation and absent such a catalyst it does not occur at an appreciable rate.

The present means for oxidizing "hydrocarbons" and carbon monoxide is by use of noble metal catalysts in the presence of sufficient oxygen for complete combustion. In practice, this requires a slight excess of oxygen such that an amount in excess of the stoichiometric

amount is provided. In addition, base metal catalysts may be used for the combustion of hydrocarbons if the operating temperature of the catalyst is raised sufficiently.

Although no catalyst is presently known for catalyzing the disproportionation of NO_x, a variety of catalysts are known which reduce NO_x to N₂, using carbon monoxide, hydrogen or hydrocarbons as the reductant. Since all three of these reductants are present in normal automobile emissions, this would appear to be a simple matter. Unfortunately, oxygen is also present in such emissions and most catalysts which reduce NO_x will not operate effectively in an oxidizing atmosphere. Instead of reducing NO_x the reductants reduce oxygen. In addition, some of the noble metals used to oxidize carbon monoxide and hydrocarbons, i.e., platinum and palladium, tend to reduce NO_x to ammonia in a highly efficient manner. Since ammonia is highly noxious, its production is undesirable. Thus, platinum and palladium either alone or in combination, are not suitable for controlling the pollutant NO_x. To avoid the production of ammonia the catalyst may be chosen as either rhodium or ruthenium, either alone or in combination, as both efficiently catalyze the reduction of NO_x to N₂. Unfortunately, the use of these catalysts create a number of problems.

Ruthenium tends to form volatile oxides in an even slightly oxidizing atmosphere and these oxides are then distilled out of the catalytic system. In addition to the resulting loss in catalytic activity, ruthenium and its compounds are highly toxic. Therefore, from a practical standpoint, only rhodium can be used for the reduction of NO_x to nitrogen. Rhodium, however, does not function as a suitable catalyst when used in an even slightly oxidizing atmosphere. Thus, there must always be excess reductant present if rhodium is to be used. Unfortunately, if too much reductant is present the reduction of NO_x to ammonia on platinum or palladium occurs. As a result of these countervailing considerations, the conversion of NO_x to nitrogen can be accomplished by rhodium only over a narrow range of oxidant and reductant, i.e., the oxidant/reductant ratio.

The above-noted oxidant/reductant ratio must be carefully controlled for the three presently known "three way" catalyst systems, i.e. platinum/rhodium; platinum/ruthenium; and monel. The narrow range of oxidant/reductant, i.e., air/fuel, under which the catalysts are operable is referred to as the "window" for the catalyst and the overall effect is referred to as the "window effect". The stoichiometric ratio of air to fuel, referred to as the air/fuel ratio or A/F ratio, is dependent on the nature of the fuel. For the fuels commonly employed for automobiles it is preferably about 14.7. When the A/F ratio is less than 14.7, the mixture is referred to as "rich", i.e., excess fuel is present in the mixture. When the A/F ratio is above 14.7 the mixture referred to as "lean", i.e., excess air or oxygen is present in the mixture. An A/F unit is simply a change in the A/F ratio of 1.0.

The three presently known "three-way" catalysts referred to above operate properly when the fuel mixture is "rich" i.e. when the A/F ratio is less than 14.7 and the environment is a reducing atmosphere. However, if the A/F ratio is much less than about 14.7 unacceptable levels of carbon monoxide and hydrocarbons pass through the catalyst unoxidized. The limits, i.e. the range of A/F values, under which the catalysts effec-

tively control all three pollutants, i.e., the "window", is between 14.4 and 14.7. When the A/F ratio moves outside these values the catalyst performance and therefore, the control of pollutants dramatically decreases. Further, below an A/F ratio of about 14.4, the formation of ammonia on the platinum catalyst becomes a significant problem.

Further, although "monel" is referred to as a "three-way" catalyst this characterization of monel is a poor one. While the platinum/rhodium and platinum/ruthenium catalysts exhibit significant oxidizing activity "monel" exhibits relatively poor oxidizing activity. "Monel" is also structurally unstable in a cycling environment, i.e., if the A/F ratio changes from rich to lean and back, as is often the case, and under this environment the catalyst deteriorates rapidly. "Monel" is also easily poisoned by sulfur which is present in small amounts in motor fuels.

Further, the efficient use of the known "three-way" catalysts requires the constant maintenance of an air to fuel ratio within 0.3 A/F units of a certain air/fuel ratio value, as determined by the particular fuel. Unfortunately, even modern carburetors cannot control the A/F ratio to within 0.3 A/F units. Therefore, the exhaust stream is constantly shifting outside the acceptable A/F ratio for efficient use of the catalyst. Further, the mixture must still be operated on a "rich" mixture which gives inherently poor fuel economy.

To circumvent the problems associated with the presently known "three-way" catalysts various engineering techniques may be employed. The use of an oxygen sensor connected in a feedback loop to a microprocessor, whereby the carburetor is controlled, is perhaps one of the better suggested methods. Unfortunately, this technique greatly increases the complexity and cost of the carburetion system and the carburetor must still operate on the "rich" side of the air/fuel mixture which inherently lessens fuel economy. Alternatively, a two-stage system may be employed wherein a first reducing stage is followed by the introduction of excess air and a second oxidizing stage. Unfortunately, this technique also increases the complexity and cost of the carburetion system and must also be operated on the "rich" side of the air/fuel mixture.

A further catalyst system is known to the prior art which although not generally thought of as a "three-way" catalyst does exhibit some "three-way" activity. This catalyst comprises an iridium-based catalyst and employs a two-stage catalyst system. The catalyst system has poor oxidizing activity, but has the advantage of operating efficiently in an oxidizing atmosphere, i.e., on a "lean" air/fuel mixture. Furthermore, the "window" for which the catalyst operates efficiently, i.e. as a three-way catalyst, is narrow, although larger than the three previously discussed, and beyond another 0.3 A/F units the NO_x reduction is relatively poor.

The above-noted catalysts all have a further inherent disadvantage. Each catalyst employs a noble metal system or iridium. These metals are extremely scarce and expensive. In particular, the scarcity and expense of rhodium, the preferred reduction catalyst, raises serious questions over its continued use as a catalyst for automobile emissions. In fact, the price of rhodium has more than doubled since 1975 and is presently about \$800.00 per troy ounce.

A preferred "three-way" catalyst would minimize the problems of presently known catalysts. Such a preferred catalyst should operate over an A/F range of up

to about 2.0 A/F units. Further, such a catalyst should operate efficiently in an oxidizing atmosphere, i.e., on the "lean" side of the air/fuel mixture wherein the A/F ratio is greater than about 14.7.

Further, it has been suggested that the oxides of nitrogen may be reduced by use of a zeolite exchanged against a catalytically active metal when said reduction is performed in the presence of an efficient amount of carbon monoxide and/or hydrogen. Such a process is disclosed in Disclosure Publication 2,411,853 of the German Federal Republic—corresponding U.S. Application, Ser. No. 340,809—wherein oxides of nitrogen are reduced in an exhaust gas comprising not more than 2% oxygen. The German disclosure has as a requirement that no more than 2% oxygen ever be present in the exhaust gas undergoing treatment. In addition, the disclosed process does not utilize the novel features of high-silica zeolites but instead utilizes zeolites such as mordenite, zeolite Y or natural zeolites such as faujasite, chabazite and erionite. Further, the disclosed process must use a nickel exchanged zeolite to minimize the production of ammonia. Further, the disclosed process requires that the amount of oxidizing gases must not be so large as to consume all reducing gas before the reduction of the oxides and nitrogen. Thus, the process requires that less than stoichiometric amounts of oxidizing gases, e.g., oxygen, be present and, as specifically claimed, the concentration of oxygen must be 2% or less.

In addition, the use of high-silica zeolites for the adsorption/combustion of an organic substrate is disclosed in co-pending U.S. application Ser. No. 053,149 filed June 29, 1979.

This co-pending application discloses another important characteristic of these high-silica zeolites, that is their ability to adsorb an organic substrate, i.e. organic compounds, until the organic substrate is catalytically acted upon. In the particular case of an gaseous exhaust stream, this characteristic provides a means of capturing and storing the organic substrate from the gaseous stream while the temperature of the stream is raised to the optimum temperature required for the catalytic process.

Further, the use of a metal containing high-silica zeolite catalyst is disclosed in co-pending U.S. Ser. No. 865,125, filed Dec. 28, 1977. U.S. Ser. No. 865,125 discloses a process for producing carbon dioxide by the conversion of hydrocarbons and carbon monoxide in a gas stream in admixture with oxygen and water vapor wherein said gas stream is contacted with a metal containing crystalline zeolite aluminosilicate. The metal is chosen from Group VIII metals. The catalyst of this co-pending application may also promote the conversion of nitric oxide to nitrogen when the gas stream is sufficiently low in oxygen such that the gas stream is essentially neutral or is reducing in the redox sense.

The present invention provides a "three-way" catalyst having advantages beyond those disclosed in the prior art.

The present invention provides a "three-way" catalyst that is relatively inexpensive in that it employs the use of a base metal, rather than a noble metal.

Further, the present invention provides a "three-way" catalyst which effectively controls emissions of carbon monoxide and hydrocarbons and provides a "three-way" catalyst wherein oxides of nitrogen are reduced preferentially to N₂ over a A/F ratio range of up to about 2.0 units.

Further, the present invention provides a "three-way" catalyst which effectively converts oxides of nitrogen to nitrogen without the production of significant amounts of ammonia, even in the absence of oxygen and with an stoichiometric excess of hydrocarbon.

Further, the present invention provides a "three-way" catalyst that is thermally stable under the conditions of oxidation and reduction and is stable in an environment that cycles from "rich" to "lean" air/fuel mixtures.

Finally, the present invention provides a "three-way" catalyst that is easily prepared, stable to handle and is virtually nontoxic.

The instant invention provides a "three-way" catalyst having the above characteristics and overcomes the difficulties of the prior art by utilizing the unusual and unexpected behavior of catalysts which employ the use of high-silica zeolites. It has been found that copper-containing high-silica zeolites provide a catalytic system for the simultaneous oxidation of carbon monoxide and hydrocarbons to essentially carbon dioxide and water and for the reduction of oxides of nitrogen to nitrogen.

The instant invention is more fully discussed hereinafter in the detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention overcomes the problems associated with those "three-way catalysts" known to the prior art by utilizing the unique behavior of copper-containing high-silica zeolites.

The novel "three-way" catalyst and process of the invention utilize the unusual properties of high-silica zeolites, i.e. those having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio which exceeds about 10 and preferably about 20. It has been found that these high-silica zeolites are organophilic and hydrophobic, and may be utilized to oxidize carbon monoxide and hydrocarbons and reduce oxides of nitrogen when they contain copper metal or copper metal ions.

It has been found that these high-silica zeolites, unlike the aluminas, maintain a relatively high adsorption capacity even at a temperature of 200° C. This behavior is to be distinguished from that of conventional zeolites, e.g. Zeolite A, U.S. Pat. No. 2,882,243; Zeolite X, U.S. Pat. No. 2,882,244; and Zeolite Y, U.S. Pat. No. 3,216,789; which tend to strongly adsorb water and only weakly adsorb an organic substrate. In addition, the thermal and hydrothermal stabilities of these high-silica zeolites are often hundreds of degrees Centigrade higher than those of conventional zeolites, i.e. in excess of 800° C.

The above-mentioned high-silica zeolites may be used so as to form "three-way" catalysts which circumvent most of the problems associated with the previously discussed catalysts. The "three-way" catalyst used herein is prepared by introducing the metal into the framework of the high-silica zeolite to form a copper-containing high silica zeolite which exhibits both unique adsorption and catalytic characteristics when used in combination with a catalytic metal. Because these high-silica zeolites have the capacity to undergo ion-exchange, the catalytic metal or metal ion may be conveniently introduced directly into the zeolite framework.

The copper-containing high-silica zeolites, i.e. three-way catalysts, of the present invention are prepared by introducing copper metal or copper ions into the high-

silica zeolite framework. As will be evident from the nature of the process and from the following examples, any zeolite or zeolite-like material having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio which exceeds about 10 and having the characteristics of these high-silica zeolites will function as the zeolite used herein. However, in order to achieve the most desirable results, the particular zeolite used herein should preferably have certain additional characteristics, as follows:

Firstly, the zeolite should be metal ion-exchanged, -doped, or loaded sufficiently so as to provide an efficient amount of catalytic metal within or on the zeolite.

Secondly, the zeolite should be thermally stable and in addition, be thermally stable in the presence of steam; that is, it should have thermal and hydrothermal stability at the temperatures at which the catalytic process occurs. Typically a thermal and hydrothermal stability of at least about 600° C. is suitable for the present invention although this value depends on the nature of the gaseous stream being combusted and the chosen process parameters, e.g. flow rate, reaction time, water content and operating temperatures.

In general, any zeolite, a crystalline material having an intracrystalline void volume, having a silica to alumina ratio greater than 10, preferably greater than 20, will be found to perform satisfactorily as the zeolite for forming the metal-containing high-silica zeolite.

Representative of those high-silica zeolites having the above-identified properties, but not limited thereto, are "silicalite", ZSM-5, ZSM-8, ZSM-11, ZSM-12, Hyper Y, ultrastabilized Y, hereinafter designated "ultra-Y", Beta, mordenite and erionite. It is to be understood that other zeolites having the properties described herein may be used without departing from the scope of the present invention. "Silicalite" is a novel crystalline silica composition having a hydrophobic/organophilic characteristic which permits its use for selectively adsorbing organic materials preferentially to water. Silicalite is more completely described in U.S. Pat. No. 4,061,724, assigned to Union Carbide Corporation. It is described in claim 1 of said patent as, "A silica polymorph consisting of crystalline silica, said silica polymorph after calcination in air at 600° C. for 1 hour, having a mean refractive index of 1.39 ± 0.01 and a specific gravity at 25° C. of 1.70 ± 0.05 g./cc." and in claim 2 as, "A silica polymorph consisting of crystalline silica, said silica polymorph after calcination in air at 600° C. for 1 hour having as the six strongest d-values of its X-ray powder diffraction pattern those set forth in Table A."

Table A is as follows:

TABLE A

d-A	Relative Intensity ^a
11.1 ± 0.20	VS
10.0 ± 0.20	VS
3.85 ± 0.07	VS
3.82 ± 0.07	S
3.76 ± 0.05	S
3.72 ± 0.05	S

^aVS = Very Strong; S = Strong

The preparation of silicalite is set forth in Examples 3, 5, 6 and 7, of U.S. Pat. No. 4,061,724, which examples are incorporated herein by reference.

The above-mentioned ZSM-type zeolites are described in various U.S. Patents and Foreign Patents as follows:

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