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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
B01D 53/94, 53/56, 53/62, B01J 37/14
A1

(11) International Publication Number: **WO 95/09687**

(43) International Publication Date: 13 April 1995 (13.04.95)

(21) International Application Number: PCT/US94/11014

(22) International Filing Date: 29 September 1994 (29.09.94)

(30) Priority Data:
08/130,340 1 October 1993 (01.10.93) US

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(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: NOBLE METAL CATALYSTS FOR THE REDUCTION OF NO_x IN THE EXHAUST GASES FROM INTERNAL COMBUSTION ENGINES CONTAINING EXCESS OXYGEN

(57) Abstract

Removal of carbon monoxide, hydrocarbons, and nitrogen oxides from the exhaust gas from lean-burn, diesel and other engines which produce exhaust gases containing excess oxygen is provided by supported noble metal catalysts which have been treated by exposure to oxygen-inert gas mixtures to provide reduction of nitrogen oxides within a particular range of engine exhaust gas temperatures. Oxidation of the remaining reducing gases is also accomplished.

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NOBLE METAL CATALYSTS FOR THE REDUCTION OF NO_x IN THE EXHAUST GASES FROM INTERNAL COMBUSTION ENGINES CONTAINING EXCESS OXYGEN

BACKGROUND OF THE INVENTION

The invention relates generally to the control of hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NO_x) in the exhaust of internal combustion engines. More particularly, the invention relates to the removal of NO_x when the exhaust gases include oxygen in excess of that needed for combustion of the fuel. This is typically the case with lean-burn engines, diesel engines, and other engines currently under development which produce such exhaust gases.

In recent years three-way catalysts have been used to remove all of the three principal noxious components in auto exhaust gases. The engines are run with stoichiometric air/fuel ratios and the catalysts are able to remove all three components at the same time, that is, a single catalyst is sufficient over the range of engine operating temperatures. More recently development of so-called "lean-burn" engines is being driven by the desire to improve fuel economy. However, such engines operate with air-fuel ratios which are far from the typical stoichiometric conditions. Instead of an air-fuel ratio of about 14.55/1 by weight, the lean-burn engine may operate with air-fuel ratios above 18/1, up to about 22-24/1, or even higher ratios for diesel engines. Compared to an engine operating with a stoichiometric air/fuel mixture, the exhaust from a lean-burn engine will include more hydrocarbons, less carbon monoxide, and less, but still excessive nitrogen oxides. While an oxidation catalyst is capable of removing hydrocarbons and carbon monoxide, since the oxygen content is high, say about 3-10% by volume, it is clear that conditions are not favorable for the reduction of nitrogen oxides. Much effort has gone into a search for catalysts which can destroy nitrogen oxides under oxidizing conditions, but the results have not been satisfactory to date.

There are two generally recognized routes to removing nitrogen oxides. First, the nitrogen oxides can be decomposed to diatomic nitrogen and diatomic oxygen. This reaction is thermodynamically favored, but catalysts which are able to carry out this reaction under the highly oxidizing conditions and high temperatures found in engine exhaust gases have not yet been found. The second route is the chemical reduction of nitrogen oxides using reducing agents present in the exhaust, such as carbon monoxide, hydrocarbons, and hydrogen. This is considered to be the mechanism of the three-way catalysts used in the exhaust from an engine operating with a stoichiometric air-fuel ratio which contains little oxygen. When a large excess of oxygen is present, as in a lean-burn or diesel engine, the oxygen can preferentially react with the hydrocarbons, carbon monoxide, and hydrogen thus removing the reducing agents needed to remove nitrogen oxides.

The use of base metals, particularly copper, ion-exchanged onto a zeolite support has been proposed by many workers in the art to be effective for reduction of nitrogen oxides. Others have suggested that such a catalyst should be combined with oxidation or three-way catalysts, usually in sequence. Toyota has proposed such arrangements in patent applications published in Japan. In JP Kokai 310742/1989 reference is made to earlier applications in which zeolites carrying transition metals are combined with downstream three-way or oxidation catalysts. These were said to be deficient and a catalyst was proposed which added noble metals to a copper-zeolite catalyst. Various methods of combining these materials are suggested. A related application is JP Kokai 127044/1989 in which an oxidation catalyst is deposited as a first layer, followed by a second layer of copper on a zeolite.

In EP 0488250A1 Toyota proposed three catalysts in series. Toyota discusses the use of various catalysts for removal of NO_x from the exhaust of lean burn engines. Pt on zeolite is useful at low temperatures and Cu on zeolite at higher temperatures, but other catalysts are shown to be useful at inlet temperatures of about 300°C. These are the noble metals combined with the oxides of rare earth metals and metals from Group IVa of the Periodic Table (earlier IUPAC), such as Ti, Zr, and Hf (Group 4 of the latest IUPAC Periodic Table).

In EP 0494388A1 the applicants disclose two stages of catalysts for first removing nitrogen oxides and then oxidizing the remaining hydrocarbons and carbon monoxide. The NO_x removal catalysts are defined as phosphates, sulfates, or aluminates of transition metals of the 4th period of the Periodic table (e.g. Cr, Mn, Fe, Co, Ni, Cu, Zn). The oxidation catalyst is generally described as a noble metal, a base metal or a perovskite on a support.

The use of more than one catalyst for the reduction of NO_x in auto exhaust gases is discussed in USSN 07/990,216 and a three-component system is proposed which is capable of operating over a range of exhaust gas temperatures. This patent application and others such as have been discussed above employ more than one catalyst because, in contrast with the behavior of three-way catalysts, the reduction of NO_x generally has been found to take place over a fairly narrow temperature range. Thus, to obtain the needed reduction over a wide range of operating temperatures more than one catalyst has been used. The present inventors have discovered that with noble metal catalysts the operating temperature "window" can be adjusted so that the full operating range can be accommodated, preferably, even with the same nominal catalyst composition.

SUMMARY OF THE INVENTION

Generally, the invention is a process for removing carbon monoxide, hydrocarbons, and nitrogen oxides from the exhaust gases produced by an engine which is operated with an excess of air relative to that required for stoichiometric combustion of the fuel, such as lean-burn, diesel, and the like. Noble metal catalysts are used which are treated in an oxygen-inert gas mixture at a temperature of at least 400°C, preferably 600° up to 1200°C, to adjust the temperature window for nitrogen oxide conversion to a desired value by varying the oxygen partial pressure. More than one catalyst may be used, each having been treated so that in combination they are able to reduce nitrogen oxides over the full range of engine exhaust gas temperatures. The reducing agents such as carbon monoxide, hydrocarbons and hydrogen can also be oxidized while the nitrogen oxides are reduced.

Preferably, the noble metals are selected from the group of platinum, and rhodium, particularly platinum-rhodium and platinum alone. The noble metals typically will be supported, preferably on an alumina or an alumina containing a rare earth metal oxide, particularly ceria, or an alkaline earth metal compound such as a sulfate, oxide, carbonate, or hydroxide. Other supports may be used, such as the oxides of Zr, Si, Ti and Sn, and cordierite or silicon carbide.

Steam is generally included in the gas mixture at about 0 to 30 vol.%, the amount of oxygen is greater than zero and up to 21 vol.%, and the remainder of the treating gas is nitrogen or other inert gas. Increasing the oxygen content of the mixture increases the temperature window for nitrogen oxide reduction so that the most active catalyst is produced by exposing the catalyst to inert gas containing substantially no oxygen with lesser activity being obtained by increasing the amount of oxygen. Preferably, the catalysts are disposed to contact the exhaust gases in order of increasing activity for NO_x reduction.

In one embodiment, the invention is at least one catalyst treated as described above.

Brief Description of the Drawings

Figure 1 is a plot of NO conversion versus temperature for Pt/Rh catalysts, showing the effect of varying oxygen content.

Figure 2 is a plot of NO conversion versus temperature for a composite catalyst of the invention showing a wide conversion window for NO.

Figure 3 is a plot of NO conversion versus temperature comparing the effect of inert gas versus air treatment.

Figure 4 is a plot of NO conversion versus temperature for Pt catalysts showing the effect of varying oxygen content.

Figure 5 is a plot of NO conversion versus temperature for various catalysts treated at varying temperatures in the absence of oxygen.

Description of the Preferred Embodiments

Those working in this field intend either to decompose nitrogen oxides into the elements directly or to reduce them using reducing agents under oxidizing conditions. The catalysts and catalyst systems of the present invention are considered to function by reducing the nitrogen oxides rather than decomposing them. However, that conclusion was reached based on experimental evidence and is not an essential aspect of the invention. The reaction mechanisms by which nitrogen oxides are reduced are believed to vary depending on the catalyst and the operating temperatures.

It has been discovered that catalysts may function differently depending upon the operating conditions and that each catalyst has a temperature range within which it is capable of destroying nitrogen oxides. We will refer to this temperature range as a "window" within which nitrogen oxides are converted. This is generally contrary to the experience with three-way catalysts which become active ("light-off") at a temperature of about 250° to 350°C and thereafter are able to oxidize hydrocarbons and carbon monoxide while reducing nitrogen oxides over the usual range of operating temperatures, say about 300° to 800°C. It should be noted here that auto exhaust changes its composition and its temperature as driving conditions change. Consequently, tests of auto exhaust catalysts require that a car be operated over a range of conditions which represents typical driving. Once three-way catalysts have reached operating temperature the performance is not greatly affected by the exhaust gas temperature. This is not the case with catalysts for use with engines operating in the lean-burn mode. Such catalysts typically have a temperature range over which they are effective for removing nitrogen oxides but they are ineffective at higher or lower temperatures. As will be appreciated, such a characteristic is not compatible with the usual variation in engine exhaust temperatures. Using the method of the present invention it is possible to remove nitrogen oxides from temperatures of about 200°C to 500°C.

Selection of catalysts for this difficult task requires consideration of the characteristics of each catalyst. It is believed that the chemical reactions differ with the catalyst composition and the temperature of operation. Consequently, it has not been possible heretofore to find a single catalyst capable of covering the full temperature range of lean-burn engine exhaust in the same manner as has been done with engines operating with stoichiometric air-fuel ratios. Typically, each catalyst has a temperature range within which it is effective and outside that range the conversion of nitrogen oxides is minimal. At the same time it is still necessary to remove the reducing agents including residual hydrocarbons, hydrogen, and carbon monoxide. Multiple catalysts may be employed, each capable of reducing nitrogen oxides within a particular temperature range. However, in the present invention it is possible to use a single catalyst composition but modify its performance so that it can reduce nitrogen oxides over a wider range of temperatures, thereby obtaining the effect previously achieved by combining catalysts of differing compositions.

In USSN 07/990,216 the use of alloyed noble metals from Group VIII was disclosed as useful. Heretofore, it had been thought that alloying was detrimental to catalyst performance. See, for example, J.T. Kummer, J. Phys. Chem. 1986, 90, 4747-4752. Also, sintering of the noble metal crystallites has been seen in aged auto catalysts, suggesting that loss of activity is associated with sintering of the noble metals. Typical three-way catalysts used with engines operated with a stoichiometric air/fuel ratio are prepared by impregnating supports with noble metal solutions and heating to temperatures of about 450 to 700°C. This process does and is intended to decompose the noble metal compounds and leave the metals as separate crystallites on the support. However, when operating under oxidizing conditions, it was found that alloying the noble metals provides durable catalysts for reduction of nitrogen oxides. One preferred method of alloying disclosed in USSN 07/990,216 is to hydrothermally treat the impregnated support in an atmosphere containing 3 to 30% steam, preferably about 10% steam (remainder an inert gas such as nitrogen) at temperatures of about 600° to 1200°C until the alloying is completed. We have now found that treating a catalyst with an inert gas such as nitrogen but adding oxygen causes the temperature window for nitrogen oxide reduction to be increased in proportion to the oxygen content. The use of the inert gas alone or in combination with steam generally produces the most active catalyst for nitrogen oxide conversion. Adding oxygen increases the temperature for peak conversion. This makes possible the use of a single catalyst composition to cover a wider range of temperatures than has been possible before by combining catalysts which reduce nitrogen oxides at different temperatures.

<u>Catalysts</u>

The noble metals of Group VIII include Pt, Pd, Rh, Ru, Os, and Ir (Groups 8-10 IUPAC). Generally, only Pt, Pd, and Rh are used in automobile exhaust catalysts. Preferred are Pt alone and Pt plus Rh in atomic proportions of 1/1 to 30/1. The catalysts may contain base metals. The base metals of Group VIII, namely Co, Ni and Fe, and metals of Groups IVa and IVb (Groups 4 and 14 IUPAC) such as Sn, Zr, Ti, and Pb may be included. Rare earth metals such as Ce may also be included, as well as the alkaline earth metals such as Ba, Sr, and Ca. Representative concentrations of the noble metals will be about 0.01 to 5.0 g/L, preferably 0.7 to 3.6 g/L, most preferably 1.0 to 2.5 g/L, when disposed on a typical monolithic carrier. The base metals, if present, will be about 0.01 to 40 g/L, preferably 0.1 to 15 g/L, most preferably 0.5 to 13 g/L, when disposed on a typical monolithic carrier.

It is typical of automobile exhaust catalysts that the noble metals and any base metal promoters are deposited on supports, either before or after such supports are placed on the surface of ceramic or metal monolithic carriers. The supports typically are aluminas of the various structures known in the art (e.g. gamma, delta, theta, alpha, etc.), but the supports may also be other metal oxides such as ZnO_2, SiO_2, TiO_2, SnO_2, cordierite, etc. or SiC.

Addition of the noble metals may be done by impregnation techniques familiar to those skilled in the art. Generally, these involve contacting the support with an aqueous solution of the metal (or metals) compound to be deposited and subsequently drying and heating the impregnated support to decompose the metal compounds. The concentration of the metal compounds in solution will be adjusted to provide the amount of metals in the finished catalyst. The noble metal compounds may be those used in the past, such as halogenated compounds (e.g. chloroplatinic acid, rhodium chloride), nitrates (e.g. rhodium nitrates), acetates (e.g. rhodium acetate), and sulfites (e.g. platinum sulfite acid i.e., hydroxy disulfite platinum (II) acid). Preferred noble metal compounds include rhodium chloride, rhodium nitrate, rhodium sulfite, rhodium oxalate, chloroplatinic acid, platinum oxalate, platinum ammine nitrite, and platinum sulfite.

The base metals are preferably applied by impregnation of the support with an aqueous solution of a base metal compound, such as the nitrates, acetates, sulfates, etc.

As will be seen, a conventionally prepared noble metal catalyst will have a temperature "window" for nitrogen oxide reduction which is at a relatively low temperature and which has a peak performance centered about say 250° to 300°C. When such a catalyst is treated with an oxygen-nitrogen mixture at temperatures of at least 400°C, preferably at least 600°C to about 1200°C, the temperature range of the window is increased. The most active catalyst is obtained when the treatment is carried out with only an inert gas, that is, substantially in the absence of oxygen. Although activity for nitrogen oxide reduction is retained, the activity of the catalysts is reduced and the window moves to higher temperatures as oxygen is added to the inert gas. Depending upon the amount of oxygen used, in a typical case the catalyst temperature window may be increased by 100° to 150°C. This makes possible a group of catalysts, all of the same nominal composition, which can cover a wide range of operating temperatures. The catalysts could be mixed together after treating. Preferably, they could be arranged in a sequence, with the catalyst having the highest temperature window (i.e. the least active) contacting the exhaust gases first and being disposed upstream of a catalyst having an overlapping temperature window but a lower peak temperature (i.e. more active). In other words, the catalysts are arrayed in order of increasing catalytic activity for NO_x reduction.

The treatment of the invention may be carried out with gas compositions in the range of 0-30 vol.% steam, greater than zero up to 21 vol.% oxygen, and the remainder nitrogen or other inert gas. The temperature will be in the general range of 400° to 1200°C and the treatment will be carried out for a sufficient period of time to adjust the temperature window for nitrogen oxide reduction to the desired range.

Example 1

Catalyst samples used for pretreatment in steam/nitrogen mixtures of varying oxygen content and subsequent performance measurements were removed from ceramic monoliths on which had been deposited Pt, Rh, CeO_2, $BaSO_4$, and Al_2O_3. Cylindrical cores measuring 4.75 inches in length and 1.5 inches in diameter (120 x 38 mm) were initially removed from the full size pieces, then cut in half longitudinally and subsequently aged at 1060°C for 6 hours in steam/nitrogen mixtures of varying oxygen content. After aging, smaller cylindrical shaped cores having dimensions of 0.5 inches (12.7 mm) in length and 0.876 inches (22.2 mm) in diameter were removed from the aged larger cores and were evaluated in a synthetic lean burn exhaust gas mixture. The nominal space velocity for the tests used was 60K hr^{-1}.

The catalyst was prepared by conventional preparation procedures, of the type described below. Initially a slurry is prepared by combining a CeO_2/Al_2O_3 (24 wt.%Ce) finely divided powder with a dilute nitric acid solution which also contains $BaSO_4$. The slurry is subsequently ball milled and pH adjusted with nitric acid to give a final pH of 3.75. An oval shaped cordierite monolith with a minor axis of 8 cm and a major axis of 16.8 cm, a length of 15.2 cm and having 400 square channels per square inch of facial area is dipped into the slurry. The geometric volume of the monolith is 1517 cm^3. After dipping, the excess slurry is blown out using an air gun. The slurry coated monolith is calcined in a gas-fired oven for about 1 hour at 540°C. Then platinum and rhodium are added to the monolith by dipping into an aqueous solution containing platinum in the form of chloroplatinic acid and rhodium in the form of rhodium chloride. After dipping, the excess solution is blown out with an air gun, and the monolith is dried and calcined for about an hour at 540°C. The final catalyst has a total washcoat loading of 0.165 g/cm^3 (2.7 g/in^3). The calculated composition of the catalyst is, Pt + Rh 0.706 g/L, (20 g/ft^3) at a Pt/Rh weight ratio of 5/1, Ce = 40 g/L, (1120 g/ft^3) and Ba = 7.49 g/L (212 g/ft^3).

Example 2

The catalyst of Example 1 was treated by exposure to a mixture of 10 vol.% steam, up to 90 vol.% nitrogen and varying amounts of oxygen at a temperature of 1060°C for 6 hours. The treated catalysts were tested by exposure to a synthetic exhaust gas containing 1200 ppmv NO_x, 3000 ppmv CO, 1000 ppmv H_2, 1600 ppmv propene, 20 ppmv SO_2, and 3.2 vol.% O_2, remainder nitrogen and 10 vol.% steam. The temperature was gradually increased up to a maximum of 800°C (rise 1), held at 800°C for one hour, and then cooled to 50°C and repeated (rise 2). The performance of the catalyst is shown in Figure 1 for rise 1. It can be seen that the conversion of NO_x begins at a low temperature, rises to a peak performance and then the conversion drops until above some higher temperature there is no significant conversion of NO_x. It will be evident that the effective temperature range of this NO_x reduction "window" is increased as the amount of oxygen in the treating gas is increased. Further, it is seen that the shape of the conversion vs. temperature curve is not greatly changed.

Example 3

Two composite catalysts were prepared using four individual catalyst samples as in Example 1 that had been pretreated at 1040°C in steam/nitrogen mixtures of varying oxygen content and combined sequentially to give a composite catalyst. The least active catalyst was placed at the exhaust gas inlet (i.e., the sample treated with the highest oxygen concentration) and the most active sample (i.e., the sample treated with the lowest oxygen concentration) at the exhaust gas outlet. Composite catalyst A consisted of four portions of a Pt,Rh,CeO_2,$BaSO_4$,Al_2O_3 catalyst as described in Example 1 which had been pretreated with

0.02 vol.% O_2, 0.06 vol.% O_2, 1.26 vol.% O_2 and 5.0 vol.% O_2 and arrayed in the reverse order, that is, with the samples treated with 5 vol.% O_2 first and the sample 0.02 vol.% O_2 last. Composite catalyst B consisted of the same catalyst but the four portions had been pretreated at 1040°C in steam-nitrogen mixtures containing 0 vol.% O_2, 1.26 vol.% O_2:, 5 vol.% O_2, and 21 vol.% O_2 and again arrayed in the reverse order. The test procedures of Example 2 were repeated with these composite catalysts. It is seen from the results in Figure 2 that the NO reduction performance of these composite catalysts is effective over a temperature range that covers 200° - 500°C.

Example 4

A catalyst was prepared by impregnating an aqueous solution of chloroplatinic acid and rhodium chloride onto a ceria-alumina granular support. The Pt content was about 3300 ppm by weight; the Rh content about 700 ppm by weight. The catalyst was dried and calcined in air at 600°C for 6 hr. The catalyst in this state is considered to be untreated. A portion of this material was treated at 1140°C in N_2 with 10% steam; this material is considered to be treated. NO reduction performance was determined using the same synthetic gas mixture and the same temperature program as used in Example 2. Performance of the two catalysts is shown in Figure 3. The panel labelled A shows performance during an initial temperature increase. As in Example 2, the temperature was increased to 800°C and the catalyst was maintained in the synthetic gas mixture at 800°C for one hour. The catalyst was subsequently cooled and then heated a second time in the synthetic gas. NO reduction during this second temperature increase is shown in panel B. Thus, panel B pertains to results obtained after aging the catalyst in the synthetic gas mixture which is, overall, an oxidizing gas mixture, at 800°C.

The treated catalyst is seen to possess NO conversion activity that is markedly superior to the untreated catalyst. Thus, treatment at high temperature in N_2 and steam is shown to improve NO reduction performance for this catalyst compared to a conventional preparation method. Note that the terms NO conversion and NO reduction are used synonymously since NO conversion is detected with a chemiluminescent NO_x analyzer that detects both NO and NO_2. NO oxidation to more highly oxidized oxides of nitrogen are not counted as converted NO. The high temperature treatment in N_2 and steam is believed to cause substantial sintering of the precious metal. Exposure of Pt to oxidizing conditions at 800°C is also known to cause sintering but the experimental result shown in panel B reveals this treatment to be inadequate to bring about the beneficial effect of this invention, namely the creation of a superior catalyst capable of reducing NO under oxidizing conditions.

Example 5

A platinum (II) sulfite acid solution was used to impregnate 80.0 g of α-Al_2O_3. The water was evaporated and the catalyst divided into portions. The Pt content was 2.5 wt.%. One portion was treated with 85% N_2, 5% O_2, and 10% steam at 1060°C for 6 hr. Another portion was treated with 90% N_2 and 10% steam at 1060°C for 6 hr. Catalytic performance of these two materials were determined using a synthetic exhaust gas designed to model emissions from an engine operating at an air-to-fuel ratio of 22/1. This gas mixture is comprised of 3300 ppmv propene, 1000 ppmv CO, 330 ppmv H_2, 700 ppmv NO, 7.5% O_2, 10% CO_2, and 10% steam. The temperature was gradually increased to 800°C and held at 800°C for an hour. The temperature was then lowered and then increased a second time to 800°C. NO reduction performance during the second temperature increase is shown in Figure 4. Performance was similar during the first temperature increase. It can be seen that the Pt/α-Al_2O_3 catalyst treated with 5% O_2 reduces NO at somewhat higher temperatures compared to the Pt/α-Al_2O_3 catalyst treated with only N_2 and steam.

Example 6

In order to demonstrate the sufficiency of nitrogen treatments for the synthesis of catalysts capable of reducing NOx under oxidizing conditions, six catalysts were prepared. Granules of a delta alumina manufactured by Condea were impregnated with an aqueous solution of platinum ammine nitrite, $Pt(NH_3)_2(NO_2)_2$, and rhodium chloride to obtain a catalyst containing 0.825 wt.% Pt and 549 ppm by weight Rh. After the aqueous solution was evaporated, the granular material was recovered and dried. Twenty grams of this first material was then treated with 90% N_2 and 10% steam at 400°C for 6 hr: this catalyst is defined as 5A. An additional twenty grams of this first material was treated with 90% N_2 and 10% steam at 800°C for 6 hr: this catalyst is defined as 5B. A second material was made using granules of a delta alumina manufactured by Condea. This second material was impregnated with an aqueous solution containing chloroplatinic acid and rhodium chloride sufficient to yield a material containing 1.33 wt.% Pt and 670 ppm by weight Rh. After the aqueous solution was evaporated, the granular material was recovered and dried. Twenty grams of this second material was treated with 90% N_2 and 10% steam at 800°C for 6 hr: this catalyst is defined as 5C. An addition twenty grams of this second material was treated with 90% N_2 and 10% steam at 1000°C for 6 hr:

this catalyst is defined as 5D. An additional twenty grams of this second material was initially calcined in air at 600°C for 6 hr and subsequently treated with 90% N_2 and 10% steam at 1000°C for 6 hr: this catalyst is defined as 5E. A third material was made by impregnating a granular γ-Al_2O_3 with a solution of chloroplatinic acid and rhodium chloride to provide a third solid material containing 0.175 wt.% Rh and 0.876 wt.% Pt. A portion of this third material was treated in N_2 in the absence of steam at 1100°C for 6 hr: this material is defined as 5F. Catalytic performance of these 6 materials was evaluated using the gas mixture and temperature program used in Example 2. Figure 5 shows NO reduction performance during the second temperature increase. It is apparent that all six of these materials are able to reduce NO in the oxidizing environment used in these experiments.

Treatment of catalyst precursors in N_2 with or without steam is sufficient to create materials with the desired catalytic properties for NO reduction under oxidizing conditions. A variety of precursors and support materials may be employed.

CLAIMS:

1. A process for removing carbon monoxide, hydrocarbons, and nitrogen oxides from the exhaust gases of an internal combustion engine containing oxygen in excess of the stoichiometric quantity needed for complete combustion comprising contacting said exhaust gases with a supported noble metal catalyst which has been treated in an oxygen-inert gas mixture optionally including steam at a temperature of at least 400°C with an oxygen partial pressure sufficient to adjust the temperature window for nitrogen oxide reduction to a predetermined value.
2. The process of Claim 1 wherein said supported noble metal catalyst includes as the noble metals platinum and rhodium.
3. The process of Claim 1 wherein said supported noble metal catalyst includes as the noble metals platinum alone.
4. The process of Claim 1 wherein said support comprises alumina and optionally a rare earth metal oxide or alkaline earth metal compound.
5. The process of Claim 4 wherein said support comprises alumina, ceria, and barium sulfate.
6. The process of Claim 1 wherein said support comprises a member of the group consisting of SiC, ZrO_2, SiO_2, TiO_2, SnO_2, and cordierite.
7. The process of Claim 1 wherein said steam-oxygen-nitrogen mixture contains 0-30 vol.% steam, greater than zero up to 21 vol.% oxygen, and the remainder nitrogen.
8. The process of Claim 7 wherein the amount of oxygen is increased to raise the temperature at which nitrogen oxides are reduced.

9. The process of Claim 1 wherein the nitrogen oxide reduction temperature window is varied between about 200° to about 500°C.

10. The process of Claim 9 wherein said supported metal catalyst combines two or more supported metal catalysts, each having a different nitrogen oxide reduction window.

11. The process of Claim 10 wherein said supported metal catalysts contact said exhaust gases in order of increasing activity for NO_x reduction.

12. The process of Claim 11 wherein said supported metal catalysts further include as the most active catalyst for NO_x reduction a catalyst treated with an inert gas at a temperature of at least 400°C in the substantial absence of oxygen.

13. The process of Claim 1, wherein said treatment is in the range of 600° - 1200°C.

14. A supported noble metal catalyst for removing carbon monoxide, hydrocarbons, and nitrogen oxides from the exhaust gases of an internal combustion engine containing oxygen in excess of the stoichiometric quantity needed for complete combustion, said catalyst having been treated with an oxygen-inert gas mixture optionally including steam at a temperature of at least 400°C with an oxygen partial pressure sufficient to adjust the temperature window for nitrogen oxide reduction to a predetermined value.

15. A supported noble metal catalyst of Claim 14 wherein a sequence of catalysts having different nitrogen oxide reduction windows is disposed in order of increasing activity for NO_x reduction.

Figure 1

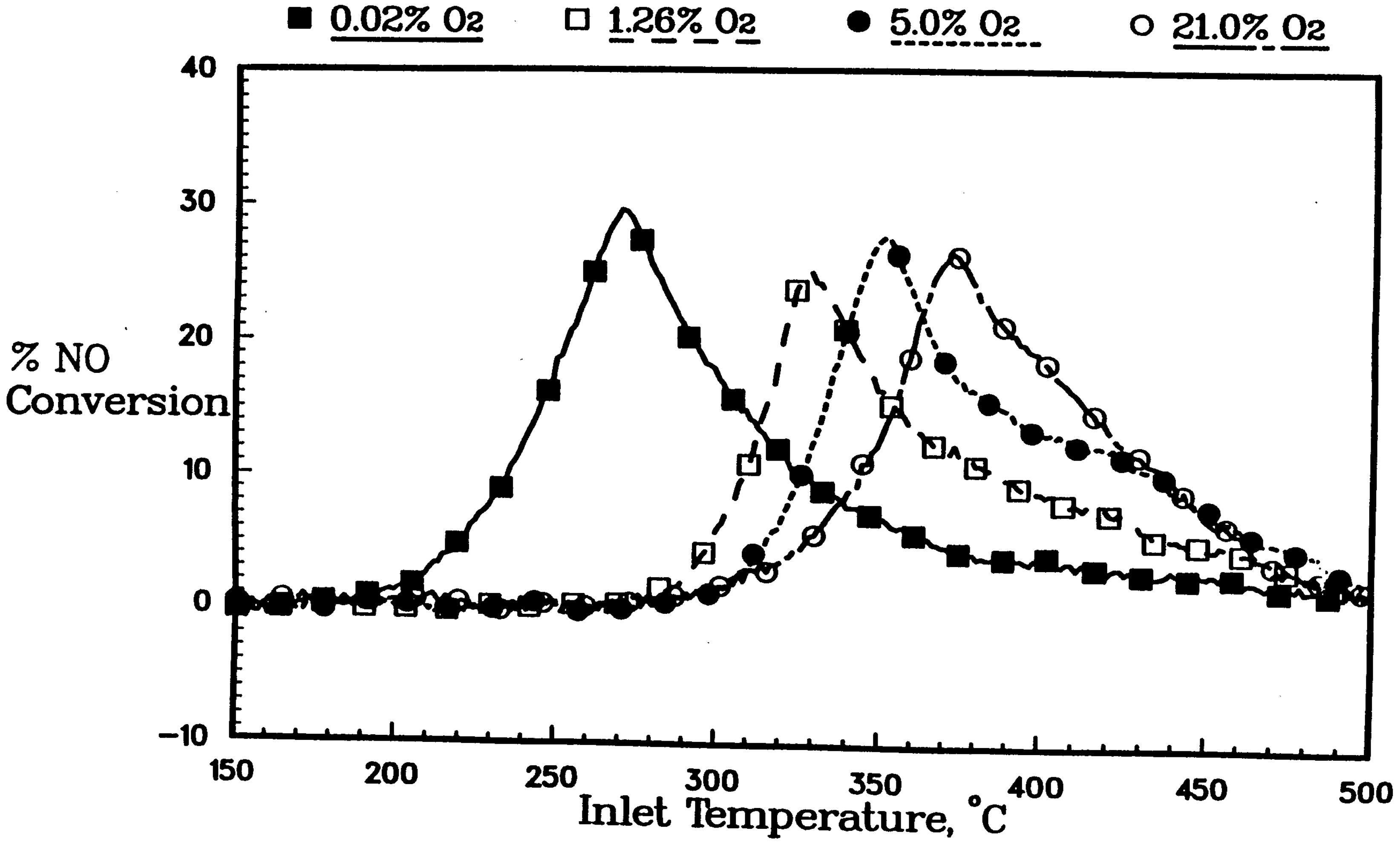

■ 0.02% O2
□ 1.26% O2
● 5.0% O2
○ 21.0% O2
% NO Conversion
40
30
20
10
0
−10
150
200
250
300
350
400
450
500
Inlet Temperature, °C

Figure 2

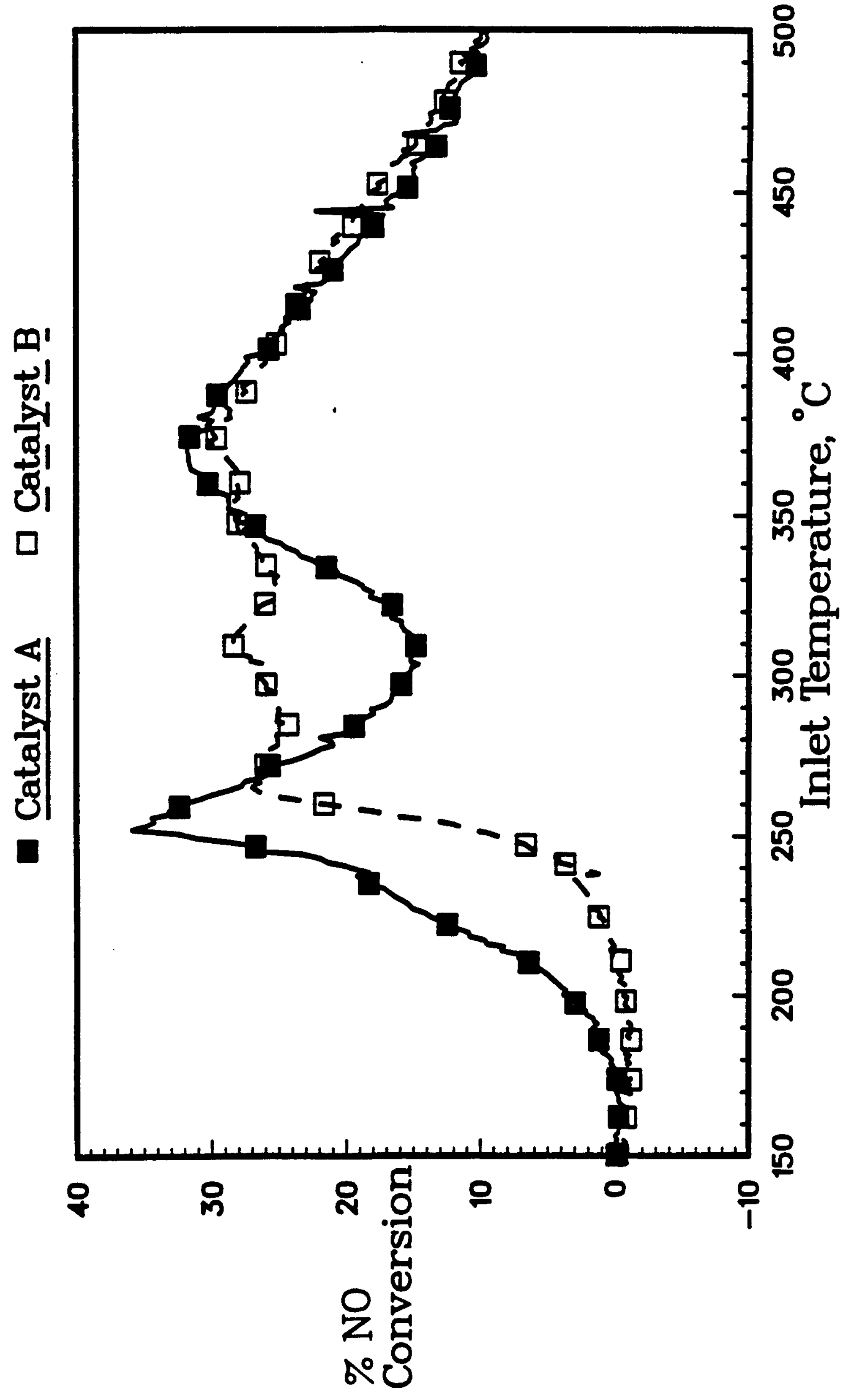

■ Catalyst A
□ Catalyst B
% NO Conversion
40
30
20
10
0
–10
150
200
250
300
350
400
450
500
Inlet Temperature, °C

FIGURE 3A

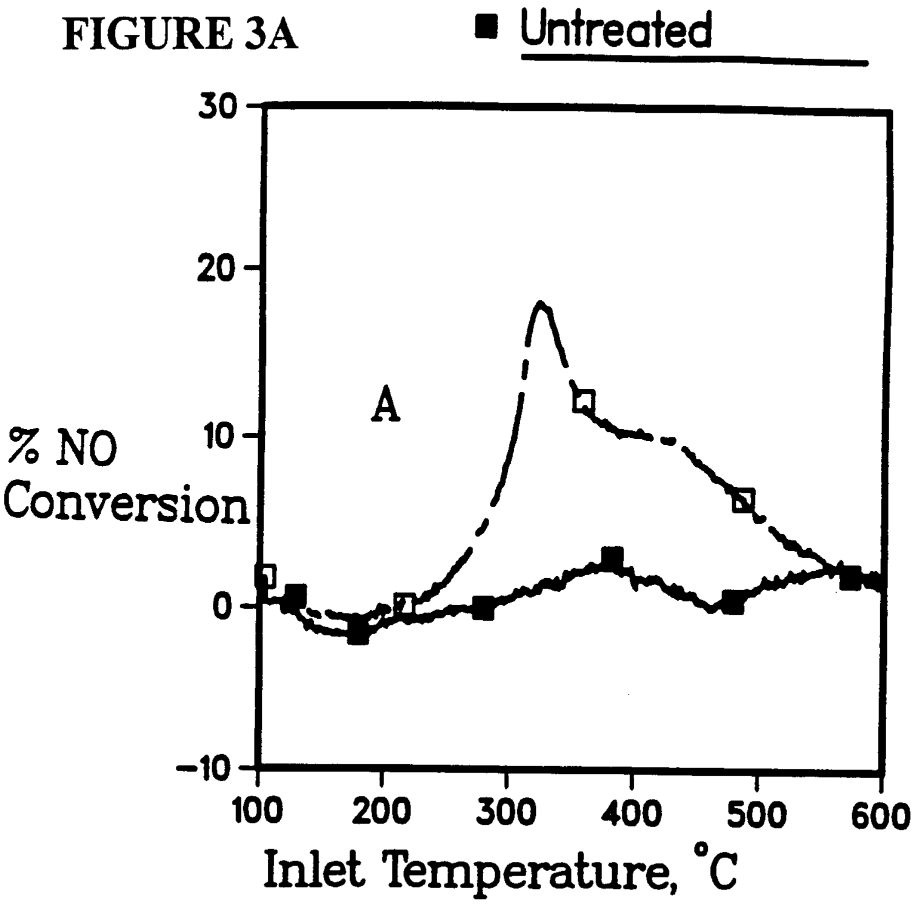


FIGURE 3B

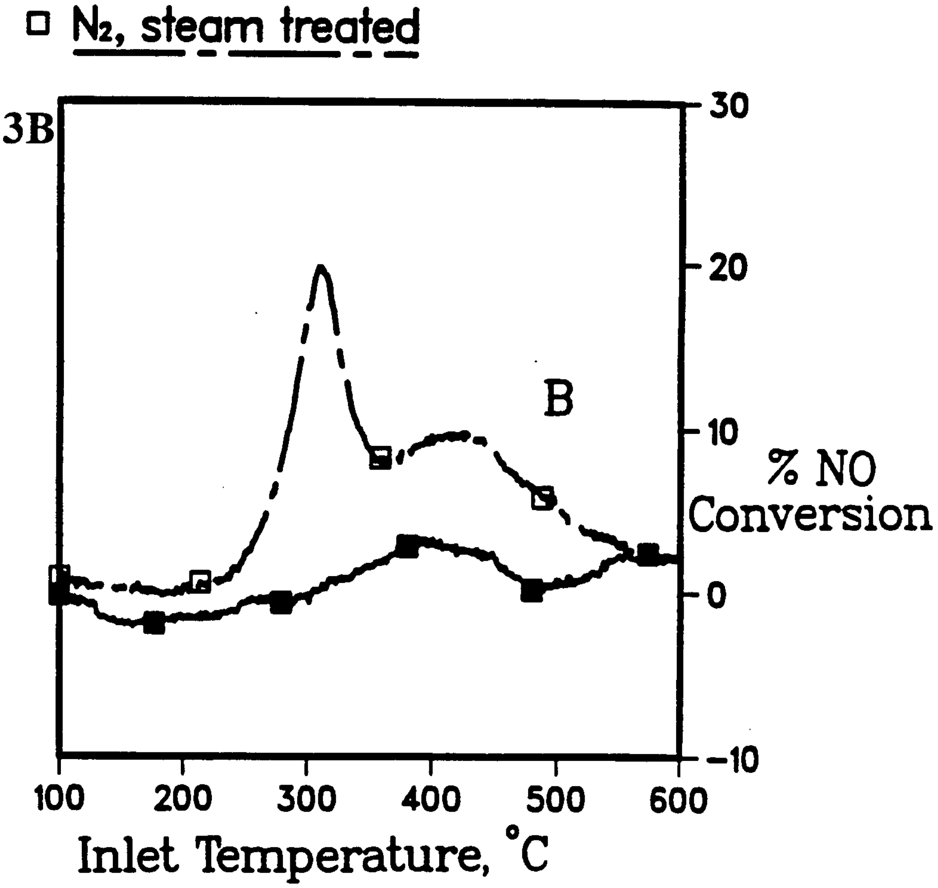


Figure 4

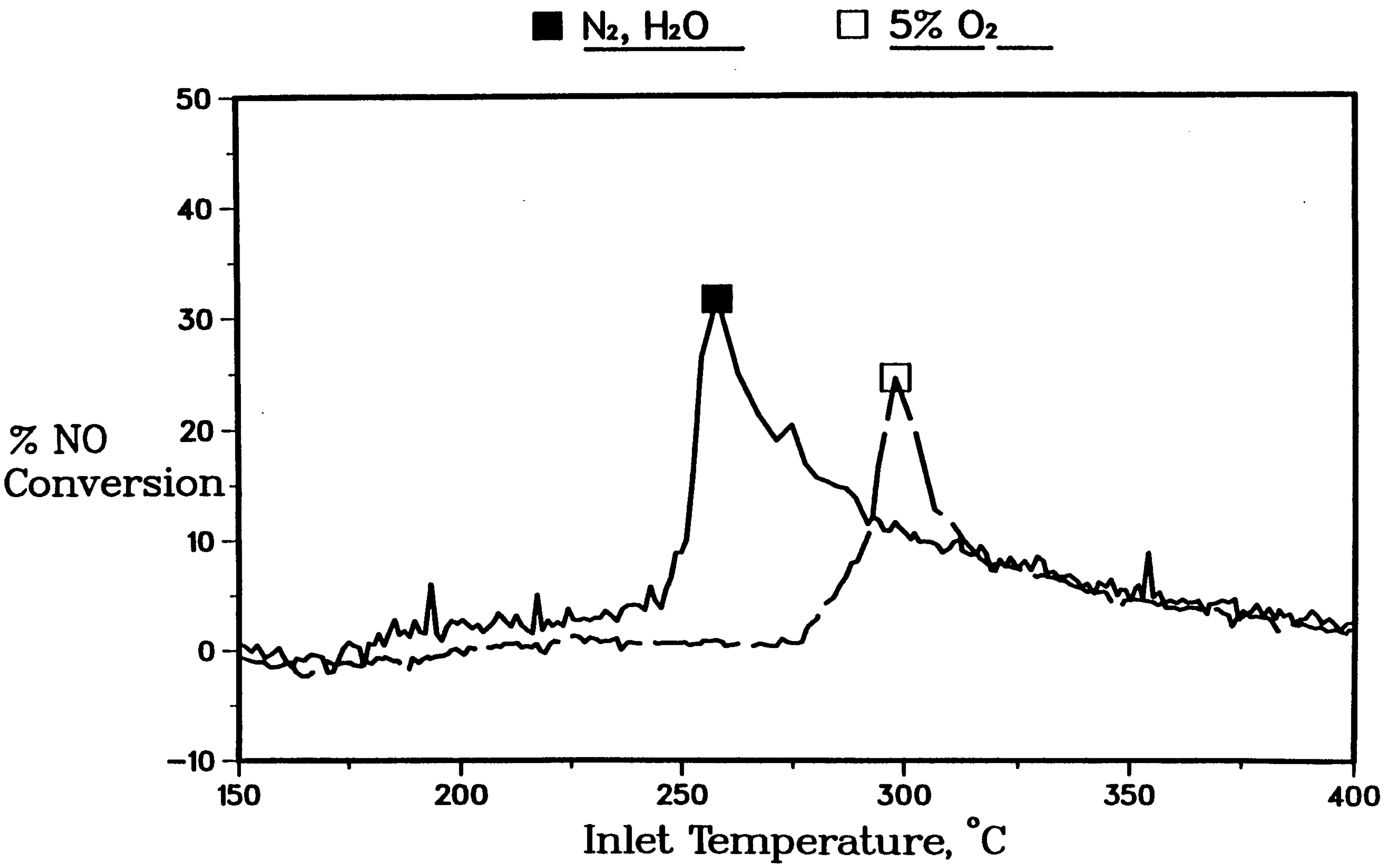
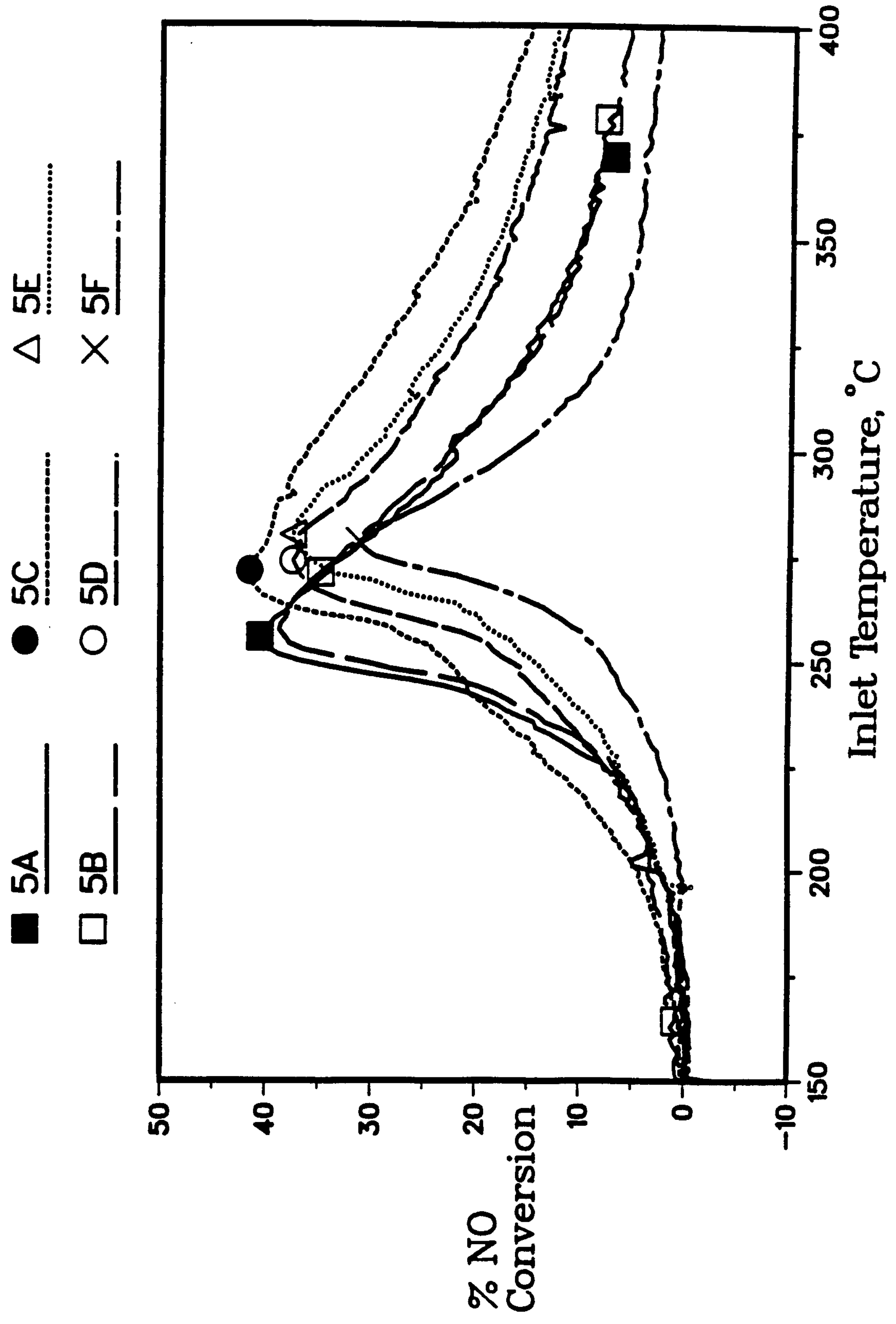

■ N_2, H_2O
□ 5% O_2
% NO Conversion
50
40
30
20
10
0
−10
150
200
250
300
350
400
Inlet Temperature, °C

Figure 5


■ 5A
□ 5B
● 5C
○ 5D
△ 5E
× 5F
% NO Conversion
50
40
30
20
10
0
−10
150
200
250
300
350
400
Inlet Temperature, °C

INTERNATIONAL SEARCH REPORT

Inten nal Application No
PCT/US 94/11014

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/94 B01D53/56 B01D53/62 B01J37/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 126 676 (PRO-CATALYSE) 28 November 1984 see page 3, line 30 - line 34 see page 6, line 11 - page 9, line 32; claim 1 ---	1-7,13, 14
A	EP,A,0 381 063 (DEGUSSA AG) 8 August 1990 see page 2, line 23 - line 46; claims 1-5; examples 1-14 ---	1-7,13, 14
A	EP,A,0 254 165 (HÜLS TROISDORF AG) 27 January 1988 see column 3, line 21 - line 44; claims 1-15 --- -/--	1-7,14

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 14 December 1994	Date of mailing of the international search report 21. 12. 94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Eijkenboom, A

INTERNATIONAL SEARCH REPORT

Inter. .al Application No
PCT/US 94/11014

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 427 494 (ENGELHARD CORP.) 15 May 1991 see claims 1-18 -----	1-6, 9-12,14, 15

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