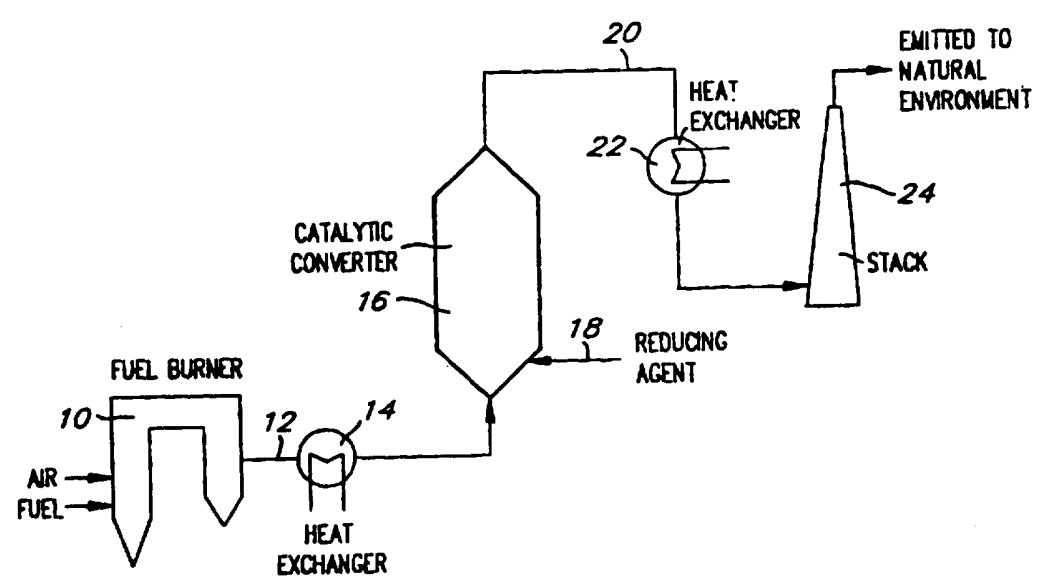




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<p>(21) International Application Number: PCT/CA96/00027 (22) International Filing Date: 19 January 1996 (19.01.96) (30) Priority Data: 2,141,734 25 January 1995 (25.01.95) CA (71) Applicant: GAZ METROPOLITAIN AND COMPANY, LIMITED PARTNERSHIP [CA/CA]; 1717 Du Havre, Montreal, Quebec H2K 2X3 (CA). (71)(72) Applicant and Inventor: PANDEY, Raj, Narain [CA/CA]; 34 Old Colony Trail, Guelph, Ontario N1G 4A9 (CA). (72) Inventors: RATNANI, Kebir; 205 De Bayeux, Boucherville, Quebec J4B 7T9 (CA). VARMA, Raghunandan, Lal; 39-125 Cole Road, Guelph, Ontario N1G 4S8 (CA). PANDEY, Rupesh, Narain; 34 Old Colony Trail, Guelph, Ontario N1G 4A9 (CA). (74) Agent: KOSIE, Ronald, S.; Brouillette Kosie, 25th floor, 1100 René-Lévesque Boulevard West, Montreal, Quebec H3B 5C9 (CA).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>

(54) Title: SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES



(57) Abstract

The selective catalytic reduction of nitrogen oxides to nitrogen is effected by reacting nitric oxide, nitrogen dioxide or a mixture thereof with a reducing agent consisting of an aliphatic carboxylic acid having 1 to 5 carbon atoms at a temperature ranging from about 250 to about 600 °C, in the presence of a catalyst comprising a metal oxide selected from the group consisting of vanadium oxide, copper oxide, nickel oxide and iron oxide, the catalyst being supported on a porous carrier. The process of the invention enables one to substantially completely reduce NO_x to harmless N₂ in an efficient, environmentally friendly and cost-effective manner.

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SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES

The present invention pertains to improvements in the emission control of environmentally harmful and regulated nitrogen oxides (NO_x) which are produced in a variety of processes such as the combustion of fossil
5 fuels. More particularly, the invention relates to an improved process for the selective catalytic reduction of nitrogen oxides to nitrogen.

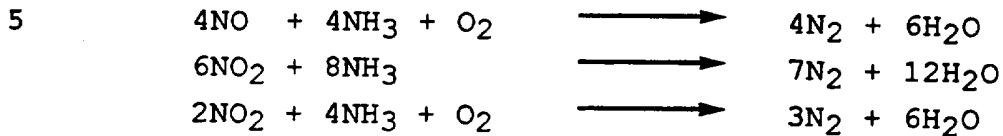
Atmospheric pollution caused by NO_x emissions has become a matter of growing global concern in recent
10 years. Nitrogen oxides contribute to acid rain and photochemical smog, and can cause respiratory problems. It is now recognized that the ground-level ozone is formed in the atmosphere through a photochemical reaction not only from volatile organic compounds but
15 also from oxides of nitrogen.

The main sources of NO_x emissions in industrialized countries are transportation, electric utilities, and industrial boilers. Much of the NO_x is a product of combustion of fossil fuels such as coal, oil
20 or gas.

Stringent regulations on NO_x emission control are currently being implemented in industrialized countries and the limit of NO_x discharge into the environment is successively being revised to place
25 increasingly effective control requirements with an ultimate goal of zero NO_x emission. In California, for instance, emission limits of 9 ppm or less have been imposed for industrial boilers above approximately 5860 kw (20 million btu/hr.)

30 Due to these stringent regulations on NO_x emissions, the development of an effective NO_x control technology has gained importance in recent years. To date, the most effective technology for controlling NO_x

emissions is the selective catalytic reduction (SCR) of NO_x . In this method, NO_x ($\text{NO} + \text{NO}_2$) are reduced by NH_3 to N_2 and H_2O , usually at $250\text{--}400^\circ\text{C}$ over a catalyst. The following reactions occur:

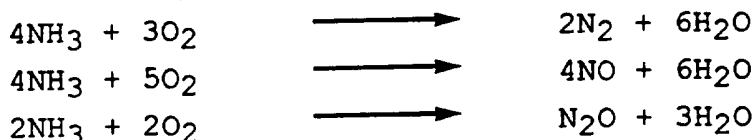


Since usually over 80 vol. % of the NO_x is in the form of NO , the first reaction is the most important. Selective catalytic reduction by NH_3 requires an ammonia injection system and an ammonia storage system. A practical disadvantage of this process is that it requires a complex and expensive set-up for safely handling NH_3 which is a hazardous chemical.

Known catalytic systems which are able to catalyze effectively the above NO_x reduction reactions using NH_3 are supported noble metals, supported base metal oxides and zeolites. Noble metal catalysts such as those based on Pt, Rh, Ru or Pd supported on Al_2O_3 or other carriers, which are used widely in catalytic converters for automobile-exhaust NO_x reduction, are usually not considered for flue gas treatment due to several drawbacks. These drawbacks include high cost, susceptibility to SO_2 poisoning and substantial reduction of the catalytic activity at high temperatures or in the presence of excess oxygen due to accumulation of adsorbed oxygen.

Catalysts based on vanadia or tungsten-vanadia as active components supported on porous anatase-type titania are currently known to be most promising for the selective catalytic reduction of NO by NH_3 mainly because of their high activity at low temperatures and

good resistance to SO₂ poisoning. These catalysts are presently used in many commercial installations. However, even with these catalysts, a number of problems are encountered. During the SCR process, NH₃ can also undergo oxidation to undesirable NO_x according to the following reactions:



When the NH₃ oxidation proceeds in parallel with SCR, it results in a greater NH₃ consumption and a lower NO_x removal efficiency. Ammonia oxidation reactions are dominant at higher temperatures (>425°C). The usual operating temperature required for SCR reaction ranges from about 300 to about 425°C for peak NO_x conversion efficiency. This temperature constraint limits the flexibility of the SCR reactor location in the integrated flue gas clean-up unit and incurs a heat exchanger cost for applications where the flue gas temperature exceeds this temperature limit. From a practical view point, the selectivity and activity of the catalysts should be retained over a broad temperature range.

Another serious disadvantage with the selective catalytic reduction of NO_x by NH₃ is the risk of unacceptably high levels of ammonia emission known as "ammonia slip". The role of ammonia in polluting the atmosphere is well known. Ammonia slip can, in principle, be suppressed by lowering the reactor inlet NH₃/NO_x ratio. This however, adversely affects the NO_x removal efficiency.

Although vanadia and tungsten-vanadia based catalysts exhibit resistance to SO₂ poisoning, they

catalyze oxidation of SO_2 to SO_3 . This latter compound
(SO_3) reacts with NH_3 and H_2O to form compounds such as
 NH_4HSO_4 and $(\text{NH}_4)_2\text{S}_2\text{O}_7$. These compounds cause
corrosion, plugging of the catalytic reactor and other
5 parts of the system, and more undesirably, plugging of
the pores of the catalysts. Pore plugging of the
catalyst eventually results in a deactivation of the
catalyst at a fixed NH_3/NO ratio and an increase of
ammonia slip. The loss in activity can be restored by
10 increasing the inlet NH_3/NO ratio. However, increasing
the NH_3/NO ratio has the effect that ammonia slip also
increases. Plugging of the catalyst pores and the
reactor can also occur due to possible formation of
 NH_4NO_3 by homogeneous reaction between NH_3 , NO_2 and
15 H_2O .

It is therefore an object of the present
invention to overcome the above drawbacks and to
provide a process for the direct and substantially
complete reduction of nitrogen oxides.

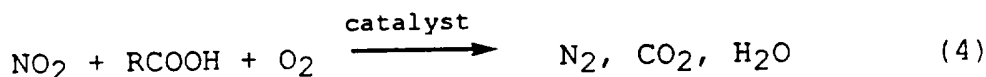
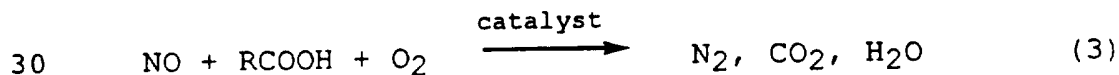
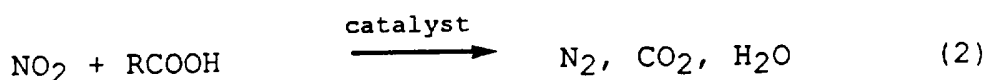
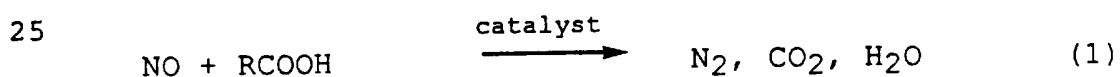
20 It is another object of the invention to provide
an improved process for the selective catalytic
reduction of nitrogen oxides, which avoids the use of a
hazardous or toxic gas.

In accordance with the present invention, there
25 is thus provided a process for the selective catalytic
reduction of nitrogen oxides to nitrogen, which
comprises reacting nitric oxide, nitrogen dioxide or a
mixture thereof with a reducing agent consisting of an
aliphatic carboxylic acid having 1 to 5 carbon atoms at
30 a temperature ranging from about 250 to about 600°C, in
the presence of a catalyst comprising a metal oxide
selected from the group consisting of vanadium oxide,

copper oxide, nickel oxide and iron oxide, the catalyst being supported on a porous carrier.

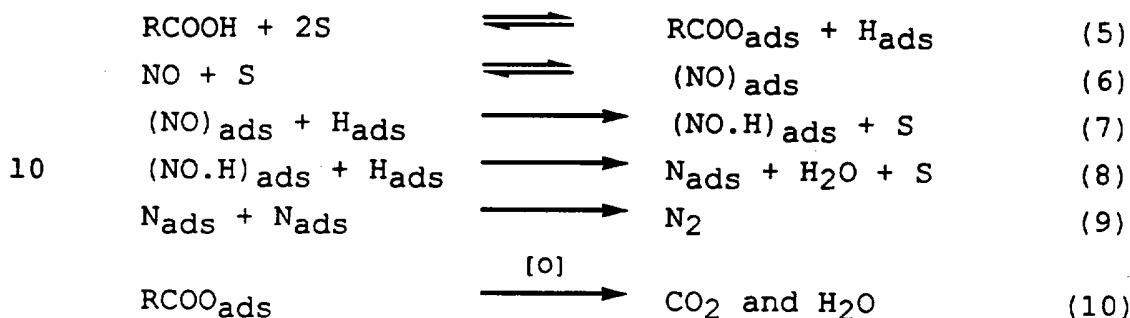
Applicant has found quite unexpectedly that by using as a reducing agent an aliphatic carboxylic acid containing 1 to 5 carbon atoms the direct and substantially complete reduction of nitrogen oxides can be achieved, provided that the reduction be carried out within the above temperature range and in the presence of the above defined catalyst.

The carboxylic acids used in accordance with the present invention, in addition to being environmentally safe, possess a very reactive or labile hydrogen atom in their structure. An oxidizing agent such as NO and NO₂ can easily abstract this labile hydrogen, forming HNO and/or HNO₂ radicals. These reactive species once formed undergo a series of reactions to produce N₂ and H₂O. The corresponding organic radicals generated from the primary decomposition of carboxylic acids readily undergo further reactions to produce CO₂ and H₂O. The catalytic reduction of NO_x with carboxylic acids ensures complete destruction of NO_x so that the final products comprise N₂, CO₂ and H₂O only. Under these conditions, complete oxidation of intermediate products occurs. The overall reactions are as follows:



where R represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

The mechanism for the selective catalytic reduction of NO_x with RCOOH is believed to be as follows:



15 where S denotes a vacant surface site and subscript 'ads' refers to an adsorbed species on the catalyst.

In addition to reactions (1)-(4), undesirable side reaction (11) could also occur, that is, RCOOH could to some extent be oxidized by O_2 (present in combustion exhaust of fuel burners) according to the following overall reaction:



25 The above defined catalysts used in the RCOOH -based selective catalytic reduction according to the invention are effective in promoting reactions (1) to (4) and suppressing the side reaction (11).

30 The loading of metal oxide on the support may vary in the range of about 5 to about 50 mole %, and more preferably in the range of about 8 to about 20 mole %. The total (BET) surface area of the catalyst may vary in the range of about 50 to about 500 m^2/g ,

and more preferably in the range of about 100 to about 300 m²/g.

The reaction is preferably carried out at a temperature of about 450 to about 500°C. Preferably, 5 nitrogen or water vapor is admixed with the reducing agent.

The process of the invention enables one to substantially completely reduce NO_x to harmless N₂ in an efficient, environmentally friendly and cost- 10 effective manner.

Further features and advantages of the invention will become more readily apparent from the following description of a preferred embodiment as illustrated by way of example in the accompanying drawing, in which:

15 Figure 1 is a flow diagram of a process for the selective reduction of nitrogen oxides according to the invention.

In the process which is schematically illustrated in Fig. 1, the NO_x containing gaseous mixture produced in the fuel burner 10 by the 20 combustion of fuel and discharged via line 12 is passed through a heat exchanger 14 for recovering most of the heat generated by the fuel combustion and lowering the temperature of the gas stream to about 250-600°C, and 25 then sent to a catalytic converter 16 containing a fixed bed of a vanadium oxide, copper oxide, nickel oxide or iron oxide based catalyst. As the NO_x containing gas stream enters into the converter 16, it is mixed with a reducing gas stream which is fed via 30 feed line 18 and contains, as a reducing agent, an aliphatic carboxylic acid having 1 to 5 carbon atoms in admixture with nitrogen and water vapor. The resulting gaseous mixture is passed through the catalyst bed

maintained at a temperature of 250-600°C and reacted with the reducing agent. The effluent stream which is discharged via line 20 and is free of NO_x contaminants is passed through a heat exchanger 22 for recovering
5 useful heat and then through a stack 24 before being discharged at a regulatory height to the natural environment.

The following non-limiting examples further illustrate the invention.

10 EXAMPLE 1

A V₂O₅/γ-Al₂O₃ catalyst containing 10 mole % V₂O₅ was prepared by impregnating γ-Al₂O₃ (10 g) with a solution of oxalic acid (4.0 g) and ammonium metavanadate (2.34 g) in distilled water (50 ml). The
15 impregnation was carried out by adding the V₂O₅/γ-Al₂O₃ to the solution followed by mixing and water evaporation. The impregnated material was further dried in an oven at 120°C for 8 hours and calcined in a muffle furnace at 500°C for 2 hours. The BET surface
20 area of the catalyst was 175 m²/g.

A quartz microreactor was packed with 0.3 g of the above catalyst and placed in a continuous flow reactor. A gaseous mixture containing nitric oxide and acetic acid was passed through the downflow reactor at
25 a flow rate of 70 ml/min. The molar composition of the feed gaseous mixture was as follows: 0.106% NO, 0.28% acetic acid, 2.15% water vapor and balance nitrogen. The reactor temperature was maintained at 435°C.

The composition of the reactor effluent was
30 analyzed by a chemiluminescence NO_x analyzer, and also by gas chromatography. The concentration of nitric oxide at various times on-stream is reported in Table 1.

TABLE 1

Time on Stream, min.	NO _x Conc. ppm	N ₂ O Conc. ppm	NO _x Conversion mole %
0	1062 ± 11	N.D.	0
15	26 ± 0.3	N.D.	97.6
35	10 ± 0.1	N.D.	99.1
60	5.5 ± 0.06	N.D.	99.5
80	3.9 ± 0.04	N.D.	99.6

N.D. = Not Detected

NO_x Detection Limit = 50 ppb

5 As it is apparent from Table 1, under a steady state, the concentration of nitric oxide was reduced from 1060 ppm to 3.9 ppm, indicating a conversion of 99.6%. The formation of other oxides of nitrogen such as NO₂ or N₂O was not detected.

10 EXAMPLE 2

The same feed mixture as in Example 1 was passed through a microreactor packed with 0.3 g of a V₂O₅/γ-Al₂O₃ catalyst containing 10 mole % V₂O₅, at 70 ml/min. flow rate. The reactor temperature was maintained at 15 445°C. The composition of the reactor effluent was analyzed in the same manner as in Example 1. The concentration of NO_x in the reactor effluent is reported in Table 2.

TABLE 2

Time on Stream, min.	NO _x Conc. ppm	N ₂ O Conc. ppm	NO _x Conversion mole %
180	1.5	N.D.	99.86

N.D. = Not Detected

As it is apparent from Table 2, the concentration of nitric oxide in the reactor effluent was 1.5 ppm, indicating a NO conversion of 99.86%. No other oxides of nitrogen such as NO₂ or N₂O were detected in the reactor effluent.

EXAMPLE 3

A gaseous mixture containing 0.62 mole % nitric oxide, 0.65 mole % acetic acid, 3.09 mole % water vapor and 95.64 mole % helium was passed through a microreactor packed with 0.3 g of a V₂O₅/γ-Al₂O₃ catalyst containing 10 mole % V₂O₅, at a flow rate of 100 ml/min. The reactor effluent was analyzed under steady state conditions. The concentration of nitric oxide in the reactor effluent at various reaction temperatures is reported in Table 3.

TABLE 3

Reactor Temp. °C	Conc. of NO in Reactor Effluent, ppm	Conc. of N ₂ in Reactor Effluent, ppm	Conversion NO mole %
375	3200	1375	48.4
450	738	2725	88.1
480	198	2993	96.8
490	73	3058	98.8
520	0	3096	100.0

As it is apparent from Table 3, in the
 5 temperature range of 375-520°C, the NO conversion
 varies in the range 48% to 100%. A corresponding
 generation of N₂ was observed, as shown by the N₂
 concentration in the reactor effluent. The conversion
 of NO in the absence of acetic acid was zero in the
 10 temperature range 375-520°C.

EXAMPLE 4

A CuO-NiO/ γ -Al₂O₃ catalyst containing 5 wt.% Cu
 and 5 wt.% Ni, calculated as metallic elements, was
 prepared by impregnating γ -Al₂O₃ (10 g) with a solution
 15 of cupric nitrate [Cu(NO₃)₂·3H₂O] (1.901 g) and nickel
 nitrate [Ni(NO₃)₂·6H₂O] (2.477 g) in distilled water
 (50 ml). The impregnated material was dried in an oven
 at 120°C for 8 hours and calcined in a muffle furnace
 at 500°C for 2 hours. The BET surface area of the
 20 catalyst was 175 m²/g. A gaseous mixture containing
 0.058 mol % (or 580 ppm) nitrogen oxides, 0.1 mol %
 acetic acid, 2.5 mol % oxygen, 16.1 mol % carbon

dioxide in nitrogen was passed through a quartz microreactor packed with 1.0 g of CuO-NiO/ γ -Al₂O₃ catalyst at a flow rate of 100 ml/min. The concentration of nitrogen oxides in the reactor effluent under steady state was monitored at various reaction temperatures, and is reported in Table 4.

TABLE 4

Reactor Temp. °C	Conc. of NO _x in Reactor Effluent, ppm	Conversion of NO _x mole %
230	55	90.5
270	6	99.0
350	190	67.2
400	312	46.2
460	391	32.6

As it is apparent from Table 4, with oxygen present in the gaseous feed mixture, the conversion of NO_x passes through a maximum in the temperature range of 230-460°C. For example, at an intermediate temperature of 270°C, the concentration of NO_x in the reactor effluent was as low as 6 ppm, representing a NO_x conversion of 99.0 mole %.

COMPARATIVE EXAMPLE

A catalyst consisting of a ZSM-5 type zeolite in protonated form having a SiO₂/Al₂O₃ ratio of 36 was prepared by crystallizing silica rich gels containing tetrapropyl ammonium bromide as template, following the procedure outlined in US Patent N° 3,702,886. The BET surface area of this catalyst was 376 m²/g. A gaseous

mixture containing 0.15 mole % nitric oxide, 0.31 mole % acetic acid, 0.95 mole % water vapor and 98.59 mole % nitrogen was passed through a microreactor packed with 0.15 g of the zeolite catalyst at a flow rate of 45 ml/min. The reactor temperature was maintained at 500°C. The reactor effluent was analyzed under steady state conditions. The concentration of nitric oxide in the reactor effluent was 0.14%, indicating a NO conversion of only 4.7%. This is much lower compared to 99% conversion obtained using V₂O₅/γ-Al₂O₃ and CuO-NiO/γ-Al₂O₃ catalysts under similar conditions.

The embodiments of the invention, in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the selective catalytic reduction of nitrogen oxides to nitrogen, which comprises reacting nitric oxide, nitrogen dioxide or a mixture thereof with a reducing agent consisting of an aliphatic carboxylic acid having 1 to 5 carbon atoms at a temperature ranging from about 250 to about 600°C, in the presence of a catalyst comprising a metal oxide selected from the group consisting of vanadium oxide, copper oxide, nickel oxide and iron oxide, said catalyst being supported on a porous carrier.
2. A process as claimed in claim 1, wherein said carboxylic acid is selected from the group consisting of formic acid, acetic acid, propionic acid and butyric acid.
3. A process as claimed in claim 2, wherein said carboxylic acid is acetic acid.
4. A process as claimed in claim 1, wherein said catalyst comprises about 5 to about 50 mole % of said metal oxide.
5. A process as claimed in claim 4, wherein said catalyst comprises about 8 to about 20 mole % of said metal oxide.

6. A process as claimed in claim 1, wherein said catalyst has a total surface area ranging from about 50 to about 500 m²/g.
7. A process as claimed in claim 6, wherein the total surface area of said catalyst ranges from about 100 to about 300 m²/g.
8. A process as claimed in claim 1, wherein said carrier is selected from the group consisting of alumina, silica and titania.
9. A process as claimed in claim 1, wherein said catalyst comprises vanadium oxide supported on γ -alumina.
10. A process as claimed in claim 9, wherein said catalyst comprises about 10 mole % of vanadium oxide.
11. A process as claimed in claim 1, wherein said catalyst comprises a mixture of copper oxide and nickel oxide supported on γ -alumina.
12. A process as claimed in claim 11, wherein said catalyst comprises about 5 wt.% Cu and about 5 wt.% Ni, calculated as metallic elements.
13. A process as claimed in claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12, wherein nitrogen or water vapor is admixed with said reducing agent.
14. A process as claimed in claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12, wherein said reaction is carried

out at a temperature ranging from about 450 to about 550°C.

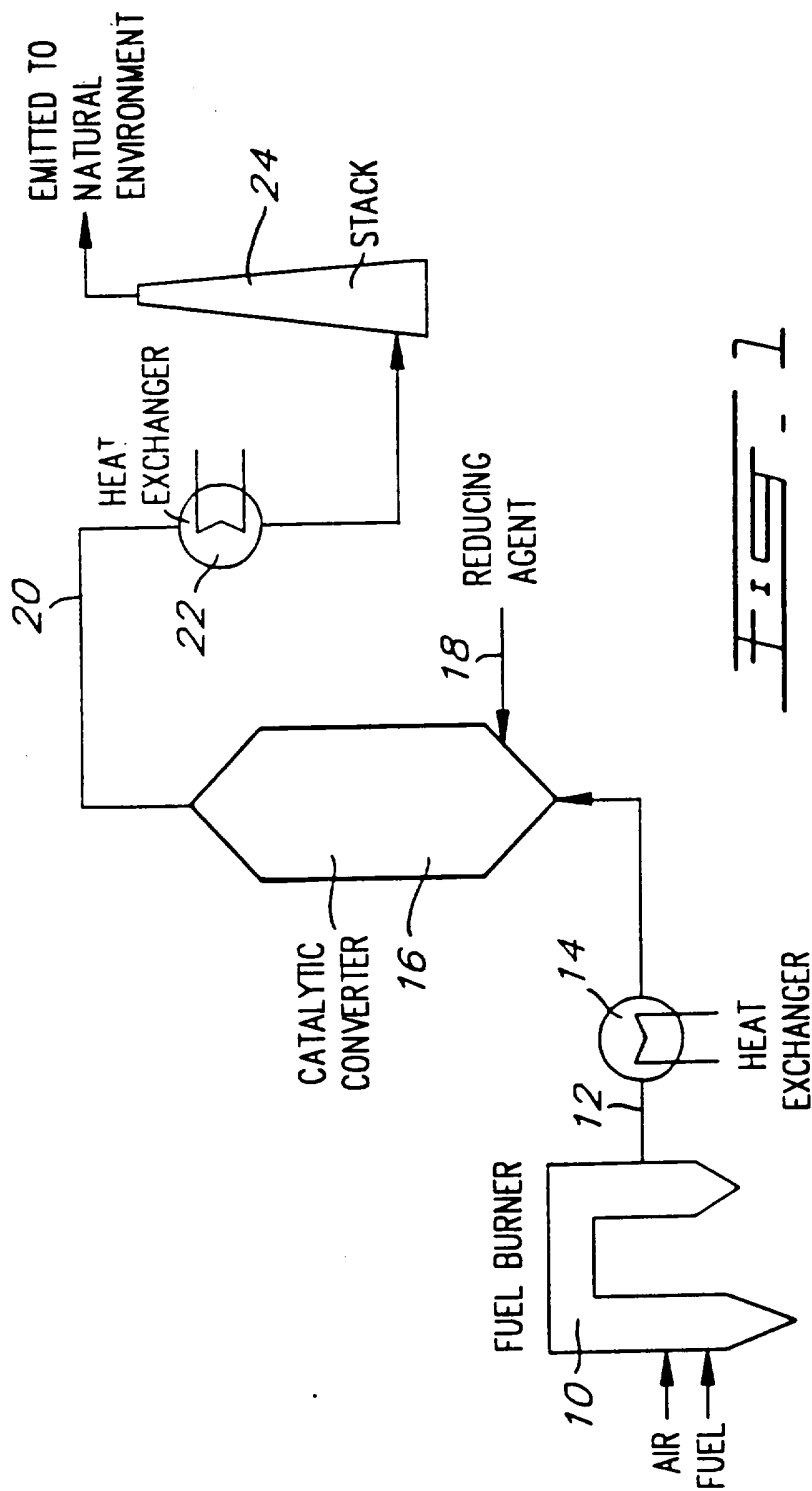


FIG. 1

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/CA 96/00027

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/56 B01D53/94 B01D53/86

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

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.
X	DATABASE WPI Section Ch, Week 9043 Derwent Publications Ltd., London, GB; Class E36, AN 90-324970 & JP,A,02 233 124 (HITACHI ZOSEN CORP) , 14 September 1990 see abstract	1-3,8,9, 14
X	DATABASE WPI Section Ch, Week 9437 Derwent Publications Ltd., London, GB; Class E36, AN 94-298918 & JP,A,06 226 052 (MITSUBISHI JUKOGYO KK) , 16 August 1994 see abstract	1,2,8

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
20 March 1996

Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 96/00027

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8009 Derwent Publications Ltd., London, GB; Class E36, AN 80-15690C & JP,A,55 008 880 (SUMITOMO HEAVY IND) , 22 January 1980 see abstract -----	1