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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{5} **:**
B01J 23/56, B01D 53/36

A1

(11) International Publication Number: **WO 94/07600**

(43) International Publication Date: 14 April 1994 (14.04.94)

(21) International Application Number: PCT/US93/08670

(22) International Filing Date: 14 September 1993 (14.09.93)

(30) Priority data:
951,969 28 September 1992 (28.09.92) US

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(81) Designated States: AU, CA, JP, KR, 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: PALLADIUM-CONTAINING THREE-WAY AUTOMOTIVE CATALYSTS HAVING UNIQUE SUPPORT

(57) Abstract

A palladium three-way catalyst is supported on a unique ceria-lanthana-alumina support where the alumina content is lower than previously believed necessary to maintain catalyst activity. Preferably the ceria and lanthana constitute the major proportion of the support.

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PALLADIUM-CONTAINING THREE-WAY AUTOMOTIVE CATALYSTS HAVING UNIQUE SUPPORT

BACKGROUND OF THE INVENTION

This invention relates to catalysts used to remove undesirable components in the exhaust gases from internal combustion engines. The exhaust from internal combustion engines contains hydrocarbons, carbon monoxide and nitrogen oxides which must be removed to levels established by government regulations. Most frequently this is done by placing catalysts in the exhaust stream which are capable of removing all three contaminants at the same time and consequently are referred to as three-way or TWC catalysts.

Maximum conversion of all three exhaust gas contaminants can be achieved by a typical TWC catalyst only when the engine is operating in a narrow range of air/fuel ratio on either side of the stoichiometric value (typically a weight ratio of 14.5/1). This optimum range is often referred to as the "A/F window". The engine is operated within the A/F window using an oxygen sensor as a reference to control the proper A/F ratio. Since the air/fuel ratio is controlled through a feed back control loop, there is a normal oscillation of the composition of the exhaust gas from rich to lean, i.e. the gases contain less or more oxygen than the target value. On the lean side, an excess of oxidants produces an oxidizing mixture and on the rich side an excess of reducing components is present.

Typical TWC catalysts contain small amounts of Group VIII metals, particularly platinum, palladium and rhodium, supported on a high surface area support such as alumina. While γ-alumina is often preferred, other forms of alumina such as delta, eta, theta, and alpha alumina may be present. Other metal oxides such as zirconia, titania, and rare earth oxides have been suggested in the art as supports. For optimum performance the TWC catalyst will often contain promoters, such as the alkaline earth metal oxides including barium, strontium, transition metals such as iron and nickel, and rare earth oxides including cerium and lanthanum. The function of these promoters is not fully understood but it is believed that they have several functions, among which is the stabilization of the supports to prevent or limit phase changes and loss of surface area.

Recently there has been a revival of commercial interest in the use of palladium in combination with or as a replacement for platinum/rhodium in TWC catalysts. The use of palladium in auto exhaust catalysts has traditionally suffered from a number of drawbacks. These include the high sensitivity of palladium to poisoning by sulphur and lead, and the reported lower catalytic efficiency of palladium. However, lead has now been removed from most gasoline supplies in the United States and Japan, and Europe is following. Thus, palladium is much more promising as a potential substitute for the platinum and rhodium used in present catalysts. Further, its much lower cost makes palladium a highly desirable alternative to platinum/rhodium in TWC catalysts, provided the desired performance can be achieved.

We have found palladium-only catalysts supported on a unique ceria-lanthana-alumina support give greatly improved performance after severe aging. It is characteristic of the support that the amount of alumina is lower than had previously been considered necessary to maintain activity. For example, in Japanese Kokai 130230/81 Nissan stated that when the amount of the rare earths exceeds 45 wt.% of the alumina that the performance deteriorates. The results show that catalysts containing 50 g/L of alumina had poorer performance than those with 100 g/L.

SUMMARY OF THE INVENTION

The present invention relates to palladium-only catalysts for automotive exhaust applications. The support has a unique ratio of cerium and lanthanum to alumina and in fact contains less alumina than has previously been thought necessary to maintain catalyst activity. Based on application of the support to a non-porous monolith, catalysts of the invention will contain less than about 100 g/L Al_2O_3 and preferably about 60 g/L or less down to about 6 g/L. In one embodiment, the amount of such as co-precipitation from a solution of all three elements (Ce, La, Al) also may be used.

Noble Metals

The noble metals from Group VIII of the Periodic Table are commonly used in auto-exhaust catalysts particularly platinum, palladium, and rhodium, either alone or in combinations. The catalysts of the invention use palladium alone although supplemental amounts of the other noble metals are not excluded if the advantages of the invention are retained. The amount of noble metals employed preferably will be about 0.01 to 10 wt.% based on the total weight of the catalyst, preferably about 0.05 to 5.0 wt.%.

The noble metals are applied to the support of the invention by decomposing a noble metal compound which has been deposited on the support. Examples of palladium compounds include chloropalladic acid, palladium chloride, palladium nitrate, diamminepalladium hydroxide and tetraamminepalladium chloride. Preferred compounds are chloropalladic acid and palladium nitrate.

The noble metals may be applied separately or in combination, but typically they will be in a solution which is used to impregnate the support by techniques familiar to those skilled in the art.

Promoters

In addition to the ceria-lanthana-alumina, the support of the invention may incorporate an alkaline earth or other promoters may be included, such as zirconium, manganese, nickel and molybdenum. In general, effective amounts of the promoters will be used, which may vary considerably. The amounts will be about 1 to 50 wt.%, preferably about 5 to 20%.

These promoter elements will be applied as decomposable compounds, usually in an aqueous solution, by methods familiar to those skilled in the art. Examples of such compounds include the halides, alumina is about 15 g/L. The catalysts will contain more than about 80 g/L Ce+La (as the metals) up to about 300 g/L. Preferably, the Ce+La content will be above 100 g/L, more preferably above 150 g/L. The weight ratio of Ce to La is also important and will be about 0.3/1 to 10/1, preferably 0.5/1 to 6/1.

In one aspect the invention includes a method for reducing carbon monoxide, hydrocarbons, and nitrogen oxides from the exhaust gases from internal combustion engines using the palladium catalysts supported on the ceria-lanthanum-alumina support just described.

Description of the Preferred Embodiments

Support

The ceria-lanthana-alumina support of the invention contains a unique ratio of these elements. It has been found that, contrary to the common belief of those skilled in the art, a support containing relatively large amounts of ceria and lanthana and an amount of alumina less than previous thought necessary to maintain activity provide exceptionally high performance, even after severe aging when used with palladium alone.

Various types of alumina may be used i.e., gamma, delta, theta, eta, etc., although delta alumina is preferred. The amount of alumina will be less than about 100 g/L on a non-porous monolithic substrate and preferably about 60 g/L down to about 6 g/L. Catalysts containing lower amounts of alumina would be expected to have poorer performance as the amount of alumina approaches zero. The amount of ceria and lanthana expressed as the metals (Ce+La) will be at least 80 g/L up to about 300 g/L preferably above 100 g/L, more preferably above 150 g/L.

The method of preparation is not believed to be critical. Generally, a finally-divided alumina may be combined with a solution of cerium and lanthanum compounds and thereafter dried and calcined at temperatures of about 100° to 600° C to form the support. Other methods nitrates, and acetates, preferably the acetates. After calcining at a temperature of about 400°C to about 700°C for about 1 to 3 hours, the promoter elements will be present as their metal oxides.

Catalyst Preparation

Catalysts of the invention may be prepared by methods known to those skilled in the art and have in common the use of the unique support of the invention for noble metals and promoters.

The support may be reduced by milling to a suitable size as required to provide particles of about 1 μm to 50 μm and then dried at a temperature of about 100°C to 600°C to produce a powder suitable for washcoating a relatively non-porous substrate. Following this step the powder may be slurried in water or other suitable liquid and the substrate immersed, sprayed, or otherwise covered with the slurry. The substrate preferably will be a monolith of the type commonly used in commercial practice. Although not preferred, non-porous pellets could be coated with the support in a similar manner with similar proportions of ceria, lanthana, and alumina. Upon drying, the substrate is then ready to receive the active catalytic metals and promoters.

Alternatively, the support may be impregnated or otherwise have the active catalytic metals and promoters deposited before the slurry is made up and the substrate coated.

In either case, the noble metals and promoters may be applied to the support by methods familiar in the art. In particular, it is preferred to apply them by co-impregnation. The order of application of these metals is not believed to be an essential aspect of the invention.

Example 1

(Comparative)

Two catalysts were prepared in which the amount of alumina was varied and the ratio of Ce+La to Al_2O_3 was the same. The supports were applied in a slurry as washcoats to a monolith carrier and then the coated monolith was impregnated with a Pd solution.

A powdered alumina (Condea Puralox SCFA-90) was mixed with cerium acetate and lanthanum acetate in aqueous solutions to provide a Al_2O_3/Ce weight ratio of 1/1 and a Al_2O_3/La weight ratio of 7.35/1. The mixture was dried and calcined at 538°C for one hour. After cooling, the resulting powder was slurried in water with nitric acid and $BaSO_4$ and applied to a cordierite monolith supplied by Corning which had 62 square cells per centimeter. The volume of the test monolith was 1.7 L and the amount of the washcoat was 260 g/L with 103.7 g/L Al_2O_3. The cerium, lanthanum and barium loadings were 103.8 g/L, 14.13 g/L, and 7.42 g/L respectively. The washcoated monolith was immersed in an aqueous solution of H_2PdCl_4 and 5 wt.% sugar to provide an impregnated monolith containing 1.41 g/L Pd. It was designated Catalyst A.

A second catalyst (B) was prepared in the same manner except that the amount of Al_2O_3 was reduced and the amounts of Ce, La, and Ba were also reduced proportionally. The finished monolith contained 1.41 g/L Pd, 69.57 g/L Ce, 9.54 g/L La, 4.94 g/L Ba, and 69.57 g/L Al_2O_3.

The catalysts were tested by exposing each sample to the exhaust gas from an engine operated at and near stoichiometric condition with test conditions intended to provide accelerated aging of the catalysts.

A Ford 5 liter V-8 engine having throttle body fuel injection was operated for 60 seconds with a predetermined air-fuel ratio, followed by 5 seconds with no fuel so that the air-fuel ratio becomes very lean. The cycle was repeated for a predetermined period of time. The fuel was a commercial lead free premium fuel to which 15 mg Pb/gal and 2 mg P/gal and 50-150 wt. ppm of sulfur was added.

Two tests were carried out, one for 100 hours and the second under slightly more severe conditions for 150 hours.

The performance of the catalysts was determined in another test using the exhaust gases from a Ford 5 liter V-8 engine. The hydrocarbon (HC), carbon monoxide (CO), and nitrogen oxides (NO) at the catalyst outlet were measured for a series of air-fuel weight ratios which traversed the stoichiometric and near-stoichiometric region from air-fuel ratios of 15/1 to 14/1. At each nominal value, the air-fuel ratio fluctuated ±0.4 units @1 Hz. The space velocity of the gases was about 30,000 hr^{-1}. The integral performance is reported at the conversion at air-fuel ratios of 14.71, 14.66, 14.61, 14.56, 14.51, 14.46, and 14.41. The performance at stoichiometric conditions is represented at an air-fuel ratio of 14.56, while an air-fuel ratio of 14.85 is slightly lean and an air-fuel ratio of 14.25 is slightly rich. The fuel used is indolene (Amoco unleaded) with traces of Pb and P and 50-150 wt.ppm of S. The nitrogen oxides at the inlet of the catalyst was controlled at 1800 wt. ppm ±50.

The "light-off" temperature was determined by continuously raising the temperature at the inlet of the catalyst over a range at which significant activity is normally experienced. When a predetermined percentage conversion is found, the temperature at the inlet is designated the light-off temperature, in these examples 50% conversion. A Ford 5 liter V-8 engine operated with a 14.56 A/F ratio (modulating ±0.4 units @ 1 Hz) supplied the exhaust gases, which were cooled to provide the desired temperature. A continuous traverse of a range of 200°C up to 450°C at 50°/min was used, followed by a descending traverse from 460°C down to 200°C at 63°/min. The fuel was indolene with trace amounts of Pb and P and 50-150 wt. ppm S. The results of the tests are summarized in the tables below.

Table 1

	100 Hour Test			150 Hour Test		
A/F Ratio Integral Stoich	Catalyst A		Catalyst B	Catalyst A		Catalyst B
HC	97		94	97	>	92
CO	92		88	87	>	81
NOx	87		84	87	>	81
A/F = 14.85						
HC	96		93	96	>	92
CO	97		96	97		95
NOx	28		28	32		32
A/F = 14.56						
HC	98		95	98		94
CO	97		95	96	>	91
NOx	98		95	97	>	91
A/F = 14.25						
HC	64		61	66	>	48
CO	37	>	27	22	>	15
NOx	98	>	78	82	>>	44
50% Conversion	100 HOUR			150 HOUR		
HC	366		377	373		373
CO	367		378	374		375
NOx	363		374	376		379

It can be seen that the performance of Catalyst B containing only 69.57 g/L Al_2O_3 has inferior performance compared to Catalyst A containing 103.7 g/L Al_2O_3 after severe engine aging. This result is consistent with the prior belief that at least 100 g/L of alumina should be applied to a monolith in order to maintain activity after aging. However, we have found that much less alumina can be used successfully provided that the amount of ceria and lanthana is increased, as will be seen in the following examples.

Example 2

A series of catalysts were prepared as in Example 1 in which the mol ratio of Ce to La was held constant at 3.37/1, but the total Ce plus La loading was increased from about 65 g/L to about 275 g/L. The amount of alumina ranged from slightly above 100 g/L down to about 15 g/L. The testing was carried out as described in Example 1 except that the evaluation of catalyst performance after aging varied the air/fuel traverse from rich to lean conditions rather than from lean to rich as in Example 1. The lightoff test was as described in Example 1.

The catalyst had the following compositions as prepared:

Catalyst	C	D	E	I
Ce, g/L	42.38	84.75	127.1	211.9
La, g/L	12.57	25.4	37.71	62.86
Ba, g/L	5.65	5.65	5.65	5.65
Al_2O_3, g/L	107.4	84.2	61.0	14.6
Ce/La	3.37	3.37	3.37	3.37
(Ce+La)/Al_2O_3	0.51/1	1.31/1	2.70/1	18.77/1

The results of testing the Catalysts C and E after aging are given in the following tables. Both employed 100 hours of engine aging with the difference being that the test in Table 2b is somewhat more severe in exposing the catalyst bed to 50-100° C higher temperatures than the aging reported in Table 2a. In both tables the results are compared to a typical commercial 1.4 g/L Pt/Rh catalyst which is supported on a washcoat of γ-alumina containing 36.37 g/L Ce and 4.59 g/L Ba.

It can be seen that after lower temperature aging (Table 2a) the Pt/Rh TWC catalyst is slightly better than Catalyst C with regard to NO_x conversion but somewhat poorer with regard to hydrocarbon conversion. However, with more severe aging (Table 2b) Catalyst E is the most active (i.e. has a lower light off temperature) and the highest conversions at the stoichiometric air fuel ratio (14.56).

Table 2a

	Comparative Pt/Rh 5/1 @ 1.41 g/L	Catalyst C Pd-only Ce+La=65 Al_2O_3 107	Catalyst E Pd-only Ce+La=165 Al_2O_3 61
Intg. Perf.			
HC	90	92	88
CO	79	79	78
NOx	79	77	74
A/F = 14.85			
HC	94	93	92
CO	97	97	97
NOx	44	37	36
A/F = 14.56			
HC	92	95	91
CO	85	87	85
NOx	82	86	83
A/F = 14.25			
HC	47	51	44
CO	32	17	20
NOx	93 >	49	48
T50 Lightoff			
HC	386	374	346
CO	379	378	339
NOx	365	381	346

Table 2b

	Comparative Pt/Rh 5/1 @ 1.41 g/L	Catalyst C Pd-only Ce+La=65 Al_2O_3 107	Catalyst E Pd-only Ce+La=165 Al_2O_3 61
Intg. Perf.			
HC	82	94	93
CO	61 <	78	80
NOx	69 <	79	79
A/F = 14.85			
HC	93	95	95
CO	91	98	98
NOx	44	39	38
A/F = 14.56			
HC	83 <	96	95
CO	61 <	85	90
NOx	69 <	85	90
A/F = 14.25			
HC	42	53	52
CO	27	18	19
NOx	83 >	52	70
T50 Lightoff			
HC	412	367	356
CO	411	368	357
NOx	398	376	356

Example 3

A series of catalysts were made in a similar manner to that of Example 1 except that no barium was added to the washcoat. The composition of the catalysts is summarized as follows:

Catalyst	F	G	H
Ce, g/L	31.79	63.57	63.57
La, g/L	63.57	63.57	15.89
Al_2O_3, g/L	125.7	126.9	125.1
Ce/La	0.5/1	1/1	4/1
(Ce+La)/Al_2O_3	95/125	127/127	79/125

Catalyst aging and testing was carried out as described in Examples 1 and 2 except that only the more severe engine aging test was used for 100 hours. The evaluation of the aged catalyst was carried out using a traverse of air fuel ratios from lean to rich as described in Example 1. The results are shown in the following table.

It can be seen that higher Ce/La ratios improve the integral and stoichiometric (A/F = 14.56) conversions of these catalysts, especially the CO and NO_x conversion. Less effect is seen on rich and lean air/fuel ratios and on light off temperature. Although the alumina content is somewhat higher than preferred for the catalysts of the invention, the relative effect of the ratio of Ce/La is expected to apply to catalyst containing 100 g/L Al_2O_3 or less.

Table 3

	Catalyst F 1.41 g/L Pd $\frac{Ce+La}{Al_2O_3} = \frac{95}{125}$	Catalyst G 1.41 g/L Pd $\frac{Ce+La}{Al_2O_3} = \frac{127}{127}$	Catalyst H 1.24 g/L Pd $\frac{Ce+La}{Al_2O_3} = \frac{79}{175}$
Intg. Perf.			
HC	86	< 91	92
CO	67	< 74	< 77
NOx	66	69	< 75
A/F = 14.85			
HC	87	91	93
CO	92	96	97
NOx	32	31	34
A/F = 14.56			
HC	87	< 92	94
CO	70	< 78	< 83
NOx	66	69	< 78
A/F = 14.25			
HC	49	48	47
CO	13	14	14
NOx	40	43	< 41
T50 Lightoff			
HC	406	399	< 399
CO	414	407	< 402
NOx	416	409	408

Example 4

Catalyst I (Example 2) had an increased Ce plus La loading of about 275 g/L and the Al_2O_3 reduced to about 15 g/L. Catalyst I was compared to Catalyst E with Ce+La loading of 165 g/L and Al_2O_3 of 61 g/L. Catalysts E and I were aged for 75 hr. using the more severe higher temperature cycle used in Tables 2b and 3 from Examples 2 and 3. The evaluation of the aged catalyst used a traverse of air fuel ratios from lean to rich as described in Example 1. Results are shown in Table 4 for conversions at 450° and 370°C, and at two space velocities (30K and 60K/hr).

Catalyst I having higher Ce and La loadings with only 25% of the alumina loading of Catalyst E has improved rich A/F conversions over Catalyst E with equivalent integral and stoichiometric conversions. These results show that with the unique washcoat support of the invention, Pd catalysts can be formulated using lower amounts of alumina (e.g. ~15 g/L) than previously considered necessary to retain activity (i.e. ≥100 g/L).

Table 4

	% Conversion (450°C inlet, 30K/hr)		% Conversion (450°C inlet, 60K/hr)		% Conversion (370°C inlet, 30K/hr)	
	Catalyst I	Catalyst E	Catalyst I	Catalyst E	Catalyst I	Catalyst E
Integral Stoich						
HC	93	93	91	91	91	90
CO	84	85	80	81	78 <	86
NO_x	82	79	75	76	75 <	81
A/F = 14.85						
HC	94	93	93	93	91	90
CO	96	96	96	96	95	95
NO_x	33	35	34	36	31	30
A/F - 14.56						
HC	95	94	92	93	91	92
CO	94	94	90	92	83 <	94
NO_x	94	90	81	85	77 <	92
A/F = 14.25						
HC	70 >	63	68 >	63	58 >	53
CO	24	22	23	20	29	31
NO_x	90 >>	65	91 >	76	95	91
50% Conversion						
	Temperature °C					
HC	375	380				
CO	384	382				
NO_x	378	382				

Example 5

Catalyst D (Example 2) was compared to the commercial Pt/Rh TWC catalyst of Example 2 with aging using the methods previously described and with two different catalyst inlet temperatures. The results show that the catalyst of the invention (D) maintained activity better than the commercial catalyst at the higher inlet temperature, demonstrating better activity and durability.

Table 5

Integral % Conversions (450° C; 30K/h)

	760° C Aged			850° C Aged		
	HC	CO	NO_x	HC	CO	NO_x
Pt/Rh	90	79	79	82	61	69
Catalyst D	91	78	75	86	74	72

Temperature (° C); 50% conversion

	760° C Aged			850° C Aged		
	HC	CO	NO_x	HC	CO	NO_x
Pt/Rh	386	379	365	412	411	398
Catalyst D	369	370	383	355	355	359

Example 6

Catalyst E (Example 2) was compared to the commercial Pt/Rh TWC catalyst of Example 2 with aging as previously described using a severe 850° C inlet temperature. As in Example 5 the catalyst of the invention (E) demonstrated superior activity and durability.

Table 6

A/F Ratio	% Conversion (450°C Inlet)		
(Stoich +/0.15 A/F	Pt/Rh		Catalyst E
Integral Performance			
HC	92		94
CO	72	<	90
NO_x	79	<	84
A/F at 14.85			
HC	95		93
CO	97		96
NO_x	47	>	34
A/F at 14.56			
HC	93		95
CO	73	<	96
NO_x	78	<	92
A/F at 14.25			
HC	57	<	65
CO	33		33
NO_x	96		94
50% Conversion		Temperature °C	
HC	406	>	359
CO	407	>	360
NO_x	389	>	360

Example 7

A comparison was made of the sulfur tolerance of the commercial Pt/Rh TWC catalyst of Example 2 with a catalyst of the invention corresponding to Catalyst E (Example 2). The amount of sulfur (as tetra hydro thiophene added to the fuel) was increased and the exhaust gases measured according to FTP-75 (Federal Test Procedure 1975) standards on a 1987 Buick Somerset with a 2.5 liter engine. The results below show that the Pd-containing catalyst of the invention performs as well as the Pt/Rh catalyst and is no more sensitive to sulfur poisoning.

Table 7

Catalyst	Sulfur Level	Total FTP-75 Performance (g/mi)		
	ppm in fuel	HC	CO	NO_x
Pd	14	0.07	1.72	0.18
	90	0.09	2.20	0.23
	500	0.10	2.42	0.24
Pt/Rh	14	0.10	1.78	0.17
	90	0.14	2.15	0.26
	500	0.19	2.86	0.25

Engine Out Emissions: 1.20 g/mi HC; 6.80 g/mi CO; 1.50 g/mi NO_x

CLAIMS

1. A catalyst for reducing the amount of carbon monoxide, hydrocarbons, and nitrogen oxides in the exhaust gases from internal combustion engines consisting essentially of

   (a) a support disposed on a monolithic substrate, said support containing an amount of cerium and lanthanum from about 80 g/L to about 300 g/L and an amount of alumina less than about 100 g/L;

   (b) an effective amount of palladium disposed on the support of (a).

2. The catalyst of Claim 1 wherein the amount of cerium plus lanthanum is above 100 g/L.

3. The catalyst of Claim 2 wherein the amount of cerium plus lanthanum is above 150 g/L.

4. The catalyst of Claim 1 wherein the alumina content is about 60 g/L or less.

5. The catalyst of Claim 4 wherein the alumina content is about 15 g/L or less.

6. The catalyst of Claim 1 wherein the weight ratio of Ce to La is 0.3/1 to 10/1.

7. The catalyst of Claim 6 wherein the weight ratio of Ce to La is 0.5/1 to 6/1.

8. The catalyst of Claim 1 wherein palladium is about 0.05 to 5.0 wt.% based on the total weight of the catalyst.

9. The catalyst of Claim 8 wherein said palladium is about 1.4 g/L.

10. A method for reducing the amount of carbon monoxide, hydrocarbons, and nitrogen oxide in the exhaust gases from internal combustion engines comprising passing said gases at an effective temperature over the catalyst of Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 93/08670

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 B01J23/56 B01D53/36

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 5 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	WO,A,91 08827 (ALLIED-SIGNAL INC.) 27 June 1991 ---	
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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search 6 December 1993	Date of mailing of the international search report [illegible]
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 Devisme, F

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PCT/US 93/08670

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