



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>3</sup>:</b> <b>B01J 35/04; F23D 17/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> WO 81/00970 <b>(43) International Publication Date:</b> 16 April 1981 (16.04.81)
<b>(21) International Application Number:</b> PCT/US79/00813 <b>(22) International Filing Date:</b> 3 October 1979 (03.10.79) <b>(71) Applicant:</b> ACUREX CORPORATION [US/US]; 485 Clyde Avenue, Mountain View, CA 94042 (US). <b>(72) Inventors:</b> ANGWIN, Meredith, Joan; 691 Florales Drive, Palo Alto, CA 94306 (US). PFEFFERLE, William, Charles; 51 Woodland Drive, Middletown, NJ (US). <b>(74) Agents:</b> BACKUS, Richard, Elliott, et al.; 160 Sansome Street, San Francisco, CA 94104 (US).		<b>(81) Designated States:</b> BR, CH, DE, GB, JP.  <b>Published</b> <i>With international search report</i>
<b>(54) Title:</b> CATALYST COMPOSITIONS, THEIR METHOD OF FORMULATION AND COMBUSTION PROCESSES USING THE CATALYST COMPOSITIONS  <b>(57) Abstract</b>  The catalytic compositions comprise a catalytically active material which is homogeneously interspersed throughout a monolithic structure of ceramic composition. The composition is shaped into a unitary monolith which is employed as the catalyst structure. In the method the active material or materials are admixed with a ceramic material, which can be either active or inactive, in finely divided form and then shaped into the monolithic structure. The catalytic compositions are used with reactants in a combustion process.		

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"CATALYST COMPOSITIONS, THEIR METHOD OF  
FORMULATION AND COMBUSTION PROCESSES  
USING THE CATALYST COMPOSITIONS"

This invention relates to catalyst systems, compositions and methods for the formulation of such compositions. More particularly, the invention relates to catalyst systems in which the active material is homogeneously interspersed throughout a monolith structure of ceramic composition.

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Presently known catalyst systems for use in applications such as combustors employ surface active materials in the form of pure pellets of the active material, or in the form of a surface coating of the active material on substrates such as ceramics. For example, it is well known to apply a catalyst material by slip coating onto a ceramic substrate which is in a honeycomb or other suitable monolith structure. For certain applications, such as gas turbine combustors, monolithic structures are most advantageous.

10

The disadvantages and limitations of conventional monolithic catalyst systems include the problem of loss of the active material by flaking off or volatilization from the substrate with a resulting loss in catalytic activity, or the problem of a change in the mechanical properties of the structures, due to an interaction of the catalyst coating and the monolith. In certain application, e.g. in combustors for gas turbines, the flaking material can cause erosion and damage to turbine blades, or the weakened catalyst/support can undergo thermostructural failure and enter the turbine, causing damage to the blades.

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It is an object of the present invention to provide new and improved catalyst systems and compositions and methods of formulating the compositions.



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Another object is to provide a catalyst system of the type described in which the active material is an integral part of the monolith structure to obviate the problems of coating flake-off or volatilization and consequent loss of catalytic activity.

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Another object is to provide a catalyst system in which the integrity of the monolith structure is maintained during sustained combustion while obviating the problem of undesirable interaction of a catalyst metal with a substrate which results in structural weakening.

10

Another object is to provide a catalyst system which provides relatively longer operating life, especially in high temperature applications, and which provides good performance through relatively higher combustion efficiency over a long period of time.

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Another object is to provide a catalyst system which achieves relatively good catalytic activity wherein the light-off temperatures of the systems compare favorably to the light-off temperatures of catalyst systems employing noble metals.

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The invention in summary comprises a system in which the catalytic composition includes a catalytically active material which is homogeneously interspersed throughout a monolith structure of ceramic composition. The composition is shaped into a unitary monolith which is employed as the catalyst structure. In one version of the method the active material or materials are admixed with a ceramic material, which can be either active or inactive, in finely divided form and then shaped into the monolith structure which is calcined. The combustion process of the invention comprises combusting reactants in the presence of the monolithic catalytic structures.

30

The foregoing and additional objects and features of the invention will appear from the following specification in which the several embodiments are set forth.

35 The catalyst systems of the invention are comprised in general of a catalytically active metal oxide material homogeneously mixed or interspersed in a ceramic metal oxide material. The mixture can be shaped into a unitary monolith of the desired configuration. The resulting monolith is thereby



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comprised throughout of the catalytically active material to provide a catalysis system with a high degree of structural integrity and with improved performance.

- 5 In one embodiment of the invention the active material is a metal oxide which is homogeneously mixed throughout an inactive (or less active) metal oxide, which can be a mixed metal oxide.

10 Examples of the active metal oxides suitable for use in this embodiment include:

NiO

CeO<sub>2</sub>

Fe<sub>3</sub>O<sub>4</sub>

15 ZrO<sub>2</sub>

LaCrO<sub>3</sub>

Co<sub>2</sub>O<sub>3</sub>

CoAl<sub>2</sub>O<sub>4</sub>

- 20 Examples of the inactive (or less active) materials suitable for use in this embodiment include:

Zirconia Spinel

Yttria-stabilized zirconia

25 MgAl<sub>2</sub>O<sub>4</sub>

SrZrO<sub>3</sub>

CaZrO<sub>3</sub>

- 30 Examples of the catalyst systems formed by the above materials for this embodiment include:

Zirconia Spinel doped with nickel oxide (5% by weight)

Yttria-stabilized zirconia doped with nickel oxide (5% by weight)

Cerium Oxide (80% by weight) with zirconia (20% by weight)

- 35 Cerium Oxide (17% by weight) with zirconia (78% by weight) with nickel oxide dopant (5% by weight)

SrCrO<sub>3</sub> Perovskite doped with Co<sub>2</sub>O<sub>3</sub> (5% by weight)



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CaZrO<sub>3</sub> doped with Co<sub>2</sub>O<sub>3</sub> (5% by weight)

CaZrO<sub>3</sub> arc-plasma sprayed with CoAl<sub>2</sub>O<sub>4</sub> doped with MgAl<sub>2</sub>O<sub>4</sub> (5% by weight)

SrZrO<sub>3</sub> arc-plasma sprayed with CoAl<sub>2</sub>O<sub>4</sub> doped with MgAl<sub>2</sub>O<sub>4</sub> (5% by weight)

5

LaCrO<sub>3</sub> (10% by weight) with ZrO<sub>2</sub> (90% by weight)

Mg<sub>.25</sub>Ni<sub>.75</sub>Cr<sub>2</sub>O<sub>4</sub>

MgAl<sub>2</sub>O<sub>4</sub> : Fe<sub>3</sub>O<sub>4</sub>

- 10 In other embodiments of the invention the monolithic catalytic composition is of the perovskite, spinel, corundum or ilmenite crystal structure type in which primary catalytically active metal oxide materials are in intimate admixture with carriers comprising inactive or active metal oxide materials which are capable of forming ceramics. The resulting composition comprises a random  
15 interspersions of the various possible crystal structures, e.g. of the perovskites, or the spinels, or the corundum, or the ilmenite, as the case may be.

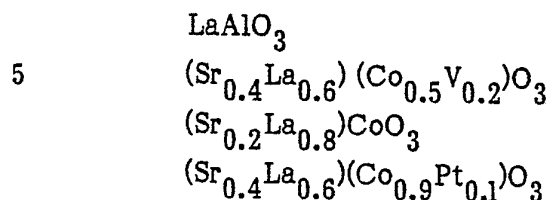
- In one such embodiment a catalytically active base metal oxide of the perovskite crystal structure ABO<sub>3</sub> forms a solid solution with another material  
20 (either active or inactive) comprising a metal oxide of the perovskite structure ABO<sub>3</sub> suitable for formation of a ceramic. Generally the perovskite structure is comprised of cations of different types of metals, one of type A and another of Type B and in which the cations are of different size with the smaller cations in the ccp array occupying the octahedral holes formed exclusively by  
25 the oxide ions.

The following are examples of the primary active perovskite base metal oxides which can be employed in this embodiment:

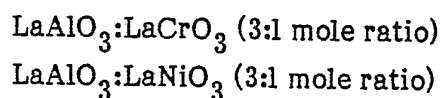
- 30 LaCrO<sub>3</sub>  
LaNiO<sub>3</sub>  
LaMnO<sub>3</sub>  
La<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub>  
La<sub>0.8</sub>K<sub>0.2</sub>Rh<sub>0.1</sub>Mn<sub>0.9</sub>O<sub>3</sub>  
35 ZrXWO<sub>3</sub> (X = Ni, Co)  
LaCoFeO<sub>3</sub>  
LaMnO<sub>3</sub> (M = Ca, or Sr)

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The following are examples of perovskite type metal oxides suitable for use as carrier materials in this embodiment:

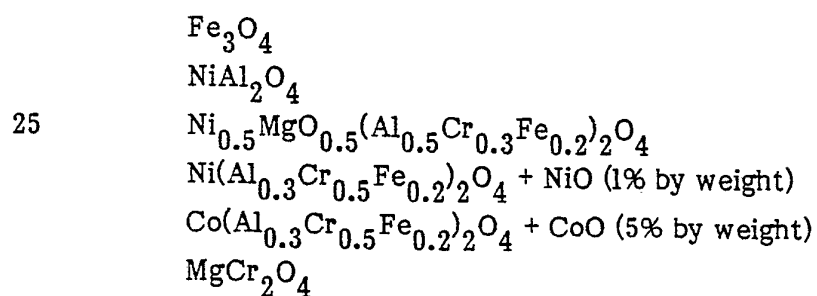


10      The following are examples of catalytically active perovskite metal oxides in solid solution with perovskite metal oxides as carriers:

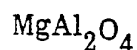


15      Another embodiment of the invention provides a primary catalytically active metal oxide of the spinel crystal structure in solid solution with a spinel structured compound which is suitable for formation of a ceramic. The spinel crystal structure takes the form  $\text{A}[\text{B}_2]\text{O}_4$  or the inverse structure  $\text{B}[\text{AB}]\text{O}_4$ .

20      The following are examples of the primary active spinel metal oxides which can be employed in this embodiment:



30      The following is an example of a spinel type metal oxide suitable for use as the carrier material in this embodiment:



35      The following are examples of the solid solutions of the catalytically active spinel materials with the carrier spinel materials:

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$$\text{MgAl}_2\text{O}_4:\text{NiAl}_2\text{O}_4 \text{ (3:1 mole ratio)}$$

$$\text{MgAl}_2\text{O}_4:\text{MgCr}_2\text{O}_4 \text{ (3:1 mole ratio)}$$

$$\text{MgAl}_2\text{O}_4:\text{Fe}_3\text{O}_4 \text{ (9:1 mole ratio)}$$

- 5 Alternatively, an oxide cermet such as the following spinel cermet example can be used:

$$\text{MgAl}_2\text{O}_4:\text{Fe}_3\text{O}_4 : (3:1 \text{ mole ratio}) + 40\% \text{ Cr by weight}$$

- 10 In another embodiment of the invention a primary catalytically active base metal oxide of either the corundum  $\text{B}_2\text{O}_3$  or ilmenite  $\text{ABO}_3$  crystal structures forms a solid solution with another material (either active or inactive) comprising a metal oxide of the corundum crystal structure suitable for formation of a ceramic.

15

Examples of the primary active corundum oxides include:

$$\text{Fe}_2\text{O}_3$$

$$\text{Co}_2\text{O}_3 \text{ stabilized with Ytria}$$

20

Examples of the primary active ilmenite oxides employed in this embodiment include:

$$\text{Cr}_2\text{O}_3$$

- 25  $\text{Fe}_x\text{Mg}_{1-x}\text{TiO}_3$  (x between 0.85 and 0.90, for example)

An example of a corundum structured compound suitable for use in this embodiment as the ceramic carrier comprises alumina.

- 30 Examples of solid solutions formed between corundum structured active compounds and the ilmenite structured carrier comprises  $\text{Cr}_2\text{O}_3:\text{Al}_2\text{O}_3$  (1:5 mole ratio) and  $\text{Fe}_{.85}\text{Mg}_{.15}\text{TiO}_3 : \text{Al}_2\text{O}_3$  (1:9 mole ratio).

- 35 Examples of solid solutions between active compounds and carriers which are both of corundum structure include:

$$\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3 \text{ (3:1 mole ratio)}$$



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$\text{Al}_2\text{O}_3 : \text{Co}_2\text{O}_3$  (5:1 mole ratio) stabilized with Yttria (2% by weight)

From the potentially large number of metal oxide compounds which could formulate into solid solutions of the foregoing type, it will be realized that those compounds containing metals with volatile oxides are generally unsuitable for combustor service. Thus, the many compounds containing barium, lead, rhenium, ruthenium, sodium and other volatile metals are not preferred. Similarly, compounds containing halogens are not considered useful for combustor service and are not preferred in this invention. Additionally, compounds of the type with known melting points below about 1873K are suitable only for lower temperature applications.

One method of formulating the catalyst systems of the invention comprises selection of the starting material in a predetermined proportion according to the mole weight formula of the composition desired for the resulting monolith structure. The starting compounds are pulverized and intermixed, such as by a ball mill or other method, to insure complete dispersion and a small particle size on the order of 10 to 20 microns. The mixture of powder is then formed into the shape which is desired for the particular ceramic technique which is to be used to form the catalyst structure. The mixture is then fired at a temperature of at least 1000° C.

As one example of a method of molding the catalyst structure to a desired shape, e.g. a honeycomb shape, would be to form an aqueous or organic slurry with the reactive powders and a binder, pour the slurry into a mold, apply heat to drive off the water and binder, and then sinter at the high temperature. Another example would be to apply a coating of such a mixture to a substrate such as paper formed into the desired shape and then burn the paper off. Another example for use where one of the starting materials is a pure compound such as alumina would be to press the powders together into the desired shape and then cause them to react.

The following is a specific example of a method of formulating a perovskite-based catalyst system which is a solid solution of  $\text{LaAlO}_3$  and  $\text{LaCrO}_3$ . Ammonium dichromate  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  is dissolved in deionized water. Added to that solution is the appropriate mole percentage of  $\text{La}_2\text{O}_3$ . Added to that mixture is a reactive alumina in the appropriate mole percentage. The



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resulting mixture is dried at about 150° C to form a sludge, then calcined at a temperature above about 600° C. The resulting powder is ball milled and than recalcined above 1300° C. A sample of the recalcined material may be checked by X-ray diffraction. If reaction is not complete, the powder is  
5 recalcined until the desired state is achieved.

At this stage the powder which has been made is a completely reacted composition of the base metal oxide. The reacted powder is ball milled with water or other suitable liquid to develop a rheology suited to the chosen  
10 forming method, then formed and shaped into the desired unitary configuration.

Another method for making materials suitable for this invention is by gelling solutions of the proper composition of the desired metals. In this case the gel  
15 may be spray-dried to provide a powder of the proper rheology for further processing.

After the powder has been brought to the proper rheology, the shaping step may be carried out by formation of a water-based slip (with appropriate organic binders and dispersants) and then casting, extruding, molding or  
20 pressing the material into the desired shape. This step may comprise coating of the slip onto a paper, polymer or sponge substrate, after which the substrate can be removed as by firing.

The final step in this method is calcining the resultant monolith material in the range of 1100-1600° C. It is preferable to calcine in an oxidizing atmosphere. However, with constituents having oxides such as  $\text{Cr}_2\text{O}_3$ , which have some volatility, it may be necessary to calcine under an inert atmosphere such as argon. If the material is calcined under a forming gas to reduce the chance of  
30 oxide vaporization, a sample of it must be checked by X-ray diffraction to make sure that segregated reduced phases have not been introduced.

The following is a specific example of a method of forming a catalyst system with a corundum-based active ceramic. In the first step appropriate mole  
35 percentages of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  and  $\text{Al}_2\text{O}_3$  (reactive) are added to deionized water using suitable dispersants. The slurry is dried at 150° C to a sludge, the sludge is calcined at a temperature of 600° C and the resulting powder is ball

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milled. The remaining steps are carried out as set forth in the above example for the perovskite-based system.

5 The following is a specific example of a method of forming a spinel-based metal oxide catalyst system which is a solid solution of  $\text{MgAl}_2\text{O}_4$  and  $\text{NiAl}_2\text{O}_4$ . Basic magnesium carbonate  $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  is dispersed in deionized water, and to that mixture are added suitable quantities of reactive  $\text{Al}_2\text{O}_3$  and  $\text{Ni}(\text{CO}_3)$ . The product is then dried at  $150^\circ \text{C}$  to a sludge, and the sludge is calcined at a temperature range of  $1000^\circ \text{C}$  -  $1300^\circ \text{C}$ . The remaining steps  
10 are carried out as in the above-described example for the method of preparing the perovskite-based system.

The following is a specific example of a method of formulating another spinel-based system which is a solid solution of  $\text{MgAl}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$ . In the first  
15 step  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  is dispersed in deionized water. To that mixture appropriate quantities of basic magnesium carbonate and reactive  $\text{Al}_2\text{O}_3$  are added as well as a dispersant. The remaining steps are carried out as described in the immediately preceding example.

20 In the method of forming catalyst systems based upon the above-described general ceramic materials, a common catalytic substrate having several percent (preferably from 1 to 10% but up to 25%) of a catalytically active metal oxide is added to the material before monolith formation. For example, nickel oxide in yttria-stabilized zirconia; nickel oxide or chromium oxide in  
25 mullite or cordierite or zircon mullite;  $\text{LaCrO}_3$  and mullite;  $\text{MgCr}_2\text{O}_4$  and alumina; or nickel oxide or  $\text{Co}_2\text{O}_3$  and alumina. The material is then shaped as described above in connection with the perovskite-based system. Longer times at calcining temperatures may be required to insure that any solid state reaction is complete during formulation.

30 Another preferred embodiment of the present invention is the use of catalytically-active oxide composition as both the catalytic and the structural materials. Although there are many advantages to be gained by mixing active materials with less-active materials, it is often desirable to use the active  
35 oxide composition for the catalytic and structural materials. An example of this is the use of  $\text{LaCrO}_3$  as the performing catalytically active, electrically-conducting monolith material.



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Example I

- Oxide powders of  $\text{MgAl}_2\text{O}_4$  and  $\text{NiAl}_2\text{O}_4$  (3:1 mole ratio) were prepared by pressing the powders into discs and calcining in the manner described above.
- 5 The disc size was 2-1/4" in diameter and 1-1/4" long with 18 to 30 holes of 0.25" diameter drilled axially to form gas flow passages. The resulting monolith structure was tested in a combustor using air and natural gas reactants under fuel-lean conditions down to a minimum preheat of 325° F. Blowout of the catalyst bed did not occur at the highest throughput attained, 849,000  $\text{hr}^{-1}$
- 10 space velocity. The catalyst was also tested on lean diesel fuel and sustained combustion to a minimum preheat of 590° F. During the diesel fuel test blowout did not occur during maximum throughput at a space velocity of 1,152,000  $\text{hr}^{-1}$ .
- 15 The results of the test of the first example are listed in Table I. CO emissions were below 50 ppm, and NO emissions ranged from 1 to 30 ppm.

Example II

- 20 Powders of  $\text{LaAlO}_3$  and  $\text{LaCrO}_3$  (3:1 mole ratio) were pressed and calcined into discs shaped as described for Example I. The catalyst was tested in a combustor using reactants of air and natural gas as well as diesel fuel. The test results are depicted in Table II.

25 Example III

- Powders of  $\text{MgAl}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  (3:1 mole ratio) were pressed and calcined into pellets shaped as described in Example I. The catalyst was tested in a combustor on lean natural gas and lean diesel fuel. The test results are set
- 30 forth in Table III.

Example IV

- Powders of  $\text{MgAl}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$  (3:1 mole ratio) were pressed and calcined
- 35 into the shape of tubes 2" in length having nominal dimensions of 1/4" OD and 1/8" ID. Forty-four of these tubes were bundled and wrapped together in insulation and supported vertically within a holder tube on a disc of Torvex



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alumina 1" long by 2" diameter which was honeycombed with 3/16" diameter cells. The catalyst structure was tested on air and lean and rich natural gas and diesel fuel. The results of the test are depicted in Table IV. The performance shows that on lean natural gas CO and NO emissions were at or below 18 and 10 ppm respectively. There was no loss in catalytic activity after 5 hours of testing.

#### Example V

10 Powders of  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  (9:1 mole ratio) were pressed and calcined into the shape of tubes 2" in length having nominal dimensions of 1/4" OD and 1/8" ID. A plurality of the tubes were bundled, wrapped together and supported in the manner described above for example IV. Platinum was added to the front segment to promote light-off. The catalyst structure was tested on air and  
15 natural gas. The results of the test are depicted in Table V.

From the foregoing it will be seen that the catalyst system compositions of the present invention provide good performance with high combustion efficiency over a long period of time. The catalytic monolith maintains its structural  
20 integrity in operation without loss of catalytic activity through flake-off or volatilization. There is no problem of interaction of base metal catalysts with the substrate, nor is there the problem of degradation of surface area due to growth in crystallite size of the active component when in operation so that there is a relatively longer life, especially in high temperature applications.

25 Additionally, the manufacturing process is relatively less expensive in that there are fewer steps to formulate the monolith structure as compared to existing techniques of manufacturing a substrate, applying a wash coat and then applying the catalyst.

30 While the foregoing embodiments are at present considered to be preferred, it is understood that numerous variations and modifications may be made therein by those skilled in the art and it is intended to cover in the appended claims all such variations and modifications as fall within the true spirit and scope of the invention.

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Test point	TA (°)	SV (1/hr)	$\dot{m}_{fuel}$ (lbm/hr)	$\dot{m}_{air}$ (lbm/hr)	$T_{ph}$ (°F)	$T_{bed}$ (°F)	Velocity (ft/sec)	CO (ppm)	NO (ppm)	UHC (ppm)	$\dot{Q}$ (Btu/hr)	Test type
41-6	191	307,000	2.36	77.4	664	2000	9.0	10	4	0	50,700	Stabilizing on natural gas
41-7					618	2025						
41-8					613	2020						
41-9					610	2020		13		1		
41-10					610	2020		10		0		
41-11					609	2010						
41-12					610				5			
41-13					608							
41-14					607	2005		8				
41-15					607	2005						
41-16					609	2005						
41-17	188	381,000	2.36	77.4	575	2010	8.6	6	5	0	50,700	Minimum pre-heat, lean, on natural gas
41-18	186	376,000		75.2	550	2010	8.7	8				
41-19	183	372,000		74.2	500	2010	8.6	8				
41-20	181	367,000		73.3	475	2005	8.5	10				
41-21	174	353,000		70.4	450		8.2		6			
41-22	172	349,000		69.4	425		8.1					
41-23	169	344,000		68.4	400		8.0	9				
41-24	162	330,000		65.5	375	2015	7.7	10	7			
41-25	160	326,000		64.5	350	2005	7.5		8			
41-26	157	321,000		63.6	325	2005	7.4		8			
41-27	152	312,000		61.6	335	2015	7.2		9			
41-34	52	219,000	4.29	38.4	523	1960	5.1	--	2	6800	92,200	Rich conditions on natural gas.
41-37	52	219,000	4.29	38.4	658	2030	5.1	--	1	3100	92,200	unstable
41-40	198	399,000	2.36	80.0	801	2035	9.2	--				
41-41	204	495,000	2.84	99.4	793	2060	11.5	--	5	0	50,700	Maximum throughput, natural gas, lean
41-42	193	545,000	3.30	109.	790	2070	12.6	43	5		61,100	
41-43	212	687,000	3.81	138.	793	2085	15.9	43	3		71,000	
41-44	249	849,000	4.02	172.	789	2025	19.7	40	2		82,000	
41-47	173	365,000	2.89	77.1	708	2090	8.5	0	16	0	62,100	Minimum pre-heat, lean, condensed fuel
41-48					692	2115		45				
41-49					663	2115		43				
41-50					642	2110		38				
41-51					626	2100		45	15			
41-52	170	356,000		75.2	603	2075	8.2	40	16			
41-53	170	356,000		75.2	596	2025	8.2	25	17			
41-58	164	356,000	2.97	75.2	876	2140	8.2	44	30	0.5	54,100	Maximum throughput, diesel fuel, lean
41-59	171	425,000	3.41	89.7	863	2200		--	--	--	62,200	
41-60	181	562,000	4.26	119.	860	2100	13.0	40	25	0.5	77,700	
41-61	168	677,000	4.92	143.	872	2260	15.7	40	23		89,700	
41-62	178	723,000	5.58	153.	878	2325	16.7	--	33		101,700	
41-63	194	883,000	6.23	186.	895	2350	20.5	13	24		113,600	
41-64	200	1,152,000	7.87	243.	867	2240	26.7	15	18		143,500	
41-65	185	1,152,000	8.53	243.	860	2340	26.7	30	21		155,500	

TABLE I

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Test point	TA (%)	SV (l/hr)	$\dot{m}_{fuel}$ (lbm/hr)	$\dot{m}_{air}$ (lbm/hr)	$T_{ph}$ (°F)	$T_{bed}$ (°F)	Velocity (ft/sec)	NO (ppm)	UHC (ppm)	Q (ntu/hr)	Test type
42-4	191	460,000	2.36	77.4	630	2120	10.6	3	0	50,700	Stabilizing on natural gas
42-5					630	2110		4	1		
42-6					630			4			
42-7					631			4			
42-8					631			5			
42-9					632			5			
42-10					634	2120		6			
42-11	191	460,000	2.36	77.4	570	2110	10.6	6	1	50,700	Minimum preheat lean, natural gas
42-12	183	442,000		75.2	548	2110	10.2				
42-13	181	437,000		73.3	525	2100	10.1				
42-14	174	421,000		70.4	500	2100	9.7	7			
42-15	169	410,000		68.4	450	2090	9.4	7			
42-16	162	393,000		65.5	425	2100	9.1	8			
42-17	157	382,000		63.6	400	2110	8.9	9			
42-18	157	382,000		63.6	377	2100	8.9	8			
42-19	52	260,000	4.29	38.4	500	2120	6.0	4	5300	92,200	Minimum preheat, rich, natural gas
42-20	56	277,000		41.3	474	2110	6.4	3	2500		
42-21	56	277,000		41.3	450	2100	6.4	3	3000		
42-22	60	293,000		44.2	390	1970	6.8	6	900		
42-23	63	284,000		46.2	375	2025	7.0	16	400		
42-25	206	589,000	1.05	99.4	690	2125	13.6	7	1	60,600	Maximum throughput, natural gas, lean
42-26	210	703,000	1.23	119.	689	2100	16.3	7		71,000	
42-27	207	789,000	1.40	133.	689	2160	18.3	7		80,600	
42-28	214	874,000	1.50	148.	691	2160	20.2	6		86,400	
42-29	184	425,000	2.66	75.5	790	2140	9.8	--	--	48,500	Minimum preheat, lean, diesel fuel
42-30					766	2140		11	4		
42-31					725	2160		12	3		
42-32					700	2160		13			
42-33	182	420,000		74.5	650	2140	9.7	12			
42-34	172	398,000		70.6	623	2150	9.2	15			
42-35	161	371,000		65.8	600	1770	8.6	20	2		
42-37	196	753,000	4.43	133.5	750	2240	17.4	12	18	80,800	Maximum throughput, diesel fuel, lean
42-38	189	944,000	5.74	167.	772	2140	21.8	18	17	10,500	
42-39	191	1,124,000	6.76	199.	792	1650	26.0	16	15	123,000	

TABLE II

Test point	TA (%)	SV (l/hr)	$\dot{m}_{fuel}$ (lbm/hr)	$\dot{m}_{air}$ (lbm/hr)	$T_{ph}$ (°F)	$T_{bed}$ (°F)	Velocity (ft/sec)	CO (ppm)	NO (ppm)	UHC (ppm)	Q (Btu/hr)	Test Type
45-2	191	395,000	2.36	77.4	770	2260	11.4	--	4	0	50,700	Stabilizing on natural gas
45-3								--	5	3		
45-4								--	5	0		
45-5								--	5			
45-6								--	4			
45-7								--	5			
45-11	191	395,000	2.36	77.4	778	2280	11.4	25	6	0	50,700	Minimum pre-heat, lean, natural gas
45-12					774	2280		20	5			
45-13					709	2250		20	4			
45-14					675	2240		25	4			
45-15	179	371,000		72.6	625	2250	10.8	0	6	2		
45-16	179	371,000		72.6	600		10.8		5			
45-17	175	362,000		70.6	595		10.5		6			
45-18	172	357,000		69.7	550	2240	10.3					
45-19	170	353,000		68.7	525	2240	10.2					
45-20	167	348,000		67.7	500	2240	10.1					
45-26	191	395,000	2.36	77.4	860	2200	11.4	0	7	0	50,700	Maximum throughput, natural gas
45-27	211	604,000	3.30	119.	824	2240	17.5		5		81,300	
45-28	214	702,000	3.78	138.	817	2250	20.3		4		87,100	
45-29	213	751,000	4.05	148.	806	2250	21.8		4			
45-30	187	388,000	2.79	80.3	794	2310	11.2	--	15	0	50,900	Minimum pre-heat, lean, diesel
45-31	182	379,000		78.4	750	2300	11.0	--	14			
45-32	182	379,000		78.4	700	2320	11.0	--	15			
45-33	182	379,000		78.4	650	2300	10.8	--				
45-34	180	374,000		77.4	625		10.6	--				
45-35	176	365,000		75.5	600		10.3	--	17			
45-36	171	355,000		73.5	575		10.3	--	17			
45-37	167	346,000		71.6	550		10.0	--	17			
45-38	162	337,000		69.7	525		9.8	--	18			
45-39	158	327,000		67.7	490	2320	9.5	--	21			
45-40	153	318,000		65.8	475	2350	9.2	--	23			
45-41	153	318,000		65.8	450	2300	9.2	--	22			
45-42	149	309,000		63.9	425	2340	8.9	--	23			
45-43	144	299,000		61.9	395	2340	8.7	--	28			
45-44	142	295,000		61.0	375	2340	8.5	--	28			
45-45	142	295,000		61.0	348	2340	8.5	--	28			
45-46	140	290,000		60.0	325	2300	8.4	--	26			
45-47	137	285,000		59.0	300	2270	8.3	--	23			
45-48	122	253,000		52.3	275	2250	7.3	--	26			
45-49	117	243,000		50.3	255	2150	7.0	--	20			
45-52	182	374,000	2.89	77.4	794	2280	10.8	--	11	2	527,000	Maximum throughput, diesel fuel
45-53	203	669,000	4.42	138.	781	2350	19.4	--	8	3	806,000	
45-54	194	814,000	5.64	168.	794	2300	23.6	--	15	2	103,000	
45-55	174	879,000	6.79	182.	793	2000	25.5	--	30	--	124,000	
45-56	140	290,000	2.79	60.0	351	2170	8.4	--	28	3	50,900	Minimum pre-heat, lean, diesel at higher throughput
45-57	119	435,000	4.92	90.0	321	2250	12.6	--	--	--	89,700	
45-58	119	435,000	4.92	90.0	304	2220	12.6	--	--	--	89,700	

TABLE III



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Test point	TA (%)	SV (1/hr)	$\dot{m}_{fuel}$ (lbm/hr)	$\dot{m}_{air}$ (lbm/hr)	$T_{ph}$ (°F)	$T_{bed}$ (°F)	Velocity (ft/sec)	CO (ppm)	NO (ppm)	HC (ppm)	Q (Btu/hr)	Test type
46-2	222	321,000	2.36	90.0	724	2450	14.9	8	4	0	50,700	Minimum preheat lean, natural gas
46-3	222	321,000		90.0	699	2450	14.9	10	5			
46-4	218	315,000		88.1	640	2450	14.6	10	7			
46-5	203	295,000		82.3	611	2400	13.7	13				
46-6	199	288,000		80.3	575	2425	13.4	13				
46-7	196	285,000		79.4	550	2350	13.2	15				
46-8	191	279,000		77.4	525	--	12.9	--	--			
46-9	187	272,000		75.5	500	2480	12.6	15	8			
46-10	182	265,000		73.5	475	2550	12.3					
46-11					450	2620						
46-12					425	2600						
46-13					400	2550		13				
46-14	179	262,000		72.6	375	2500	12.1	--				
46-15	179	262,000		72.6	350	2550	12.1	15				
46-16	179	262,000		72.6	325	2525	12.1	10				
46-17	175	255,000		70.6	300	2525	11.8	15				
46-18	175	255,000		70.6	275	2500	11.8					
46-19	175	255,000		70.6	250	2500	11.8					
46-20	170	249,000		68.7	178*	2450	11.5					
46-23	50	152,000	4.29	36.8	674	2620	7.0	--	6	6000	92,000	Unstable on natural gas, rich
46-25	234	338,000	2.36	94.8	824	2450	15.7	18	10	0	50,700	Maximum throughput, lean, natural gas
46-26	227	390,000	2.82	109.	780	2450	18.1	15	8		60,600	
46-27	212	426,000	3.27	119.	780	2400	19.7	13			70,300	
46-28	208	479,000	3.75	134.	789	2525	22.2	15			80,600	
46-29	213	530,000	4.05	145.	788	2500	24.5	10			87,100	
46-32	207	307,000	2.82	90.0	780	2550	14.2	20	7	0	60,600	Unstable on diesel fuel
46-33	207	307,000	2.82	90.0	804	2500	14.2	10	8	1	60,600	
46-35	175	472,000	5.12	139.	850	--	21.9	10	9	10	112,600	
46-37	191	279,000	2.36	77.4	525	2450	12.9	5	5	0	50,700	Still catalytically active on natural gas
46-38	191	279,000	2.36	77.4	497	2450	12.9	5	5	--	50,700	

\* Ambient

TABLE IV

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Test Point	TA (°)	SV (l/hr)	$\dot{m}_{CH_4}$ (lbm/hr)	$\dot{m}_{air}$ (lbm/hr)	$T_{ph}$ (°F)	$T_{bed}$ (°F)		CO (ppm)	NO (ppm)	HC (ppm)	Test Type
						TR1	TR2				
32-10	180	116,000	2.44	75.7	683	2520	800	20	30	8	Aging (bed nonuniform)
32-12	197	116,000	2.23		685	2600	1560	16	28	12	
32-14	207	115,000	2.12		688	2575	1775	18	22	9	
32-15					689	2575	1840	20	23	---	
32-16					688	2560	1850	20	21	---	
32-17					689	2575	1910	25	21	---	
32-18	213		2.06		690	2600	2125	19	22	---	
32-20	205	111,000		72.7	689	2590	2100	16	20	---	
32-21					690	2570	1900	16	19	---	
32-23					690	2560	1810	20	15	---	
32-24							1890	21	15	---	Minimum preheat, lean
32-25							1950	19	20	---	
32-26					691	2580	2100	21	20	1	
32-27							2110	22	18	2	
32-28						2575	1200	21	16	2	
32-29						2575	1690	20	16	2	
32-30					690	2580	1750	20	14	2	
32-31					690		1740	20	14	1	
32-32					691		1710	21	14	1	
32-33							1740	20	14	1	
32-34							1810	21	14	0	
32-35							1640	20	13	0	
32-36					690	2525	2560	4	3	1	Maximum throughput
32-41	245	123,000	1.93	81.5	778	2575	2560	5	3	0	
32-42	242	123,000	1.96		761	2560	2550	5	3	0	
32-43	235	124,000	2.01		745	2580	2560	5	3	0	
32-45	235		2.01		725	2550	2525	5	3	0	
32-47	218		2.17		698	2575	2550	5	4	0	
32-48	205		2.31		675	2600	2580	5	5	3	
32-49	205		2.11		646	2580	2560	5	4	2	
32-50	201	125,000	2.36		623	2590	2570	5	5	2	
32-51	196	125,000	2.41		599	2575	2550	5	4	3	
32-52	193	123,000	2.41	80.1	574	2570	2550	5	4	2	
32-54	190	126,000	2.52	82.5	582	2600	2590	5	5	1	
32-56	188	143,000	2.87	91.2	550	2600	2590	5	5	2	
32-57	160	126,000	2.95	81.5	500	2575	2550	6	4	0	
32-58	176	137,000		89.3	440	2560		6	4	0	
32-59	176	137,000		89.3	400	2570		6	4	0	
32-61	179	121,000	2.55	78.6	750*	2500	2490	6	4	0	
32-62	173	107,000	2.33	69.4	762*	2500	2490	6	4	0	
32-65	210	154,000	2.79	101	645	2600	2575	5	4	0	
32-66	217	219,000	3.82	144	649		--	6	4	0	
32-67	216	229,000	4.05	150	656		--	6	4	0	
32-68	218	232,000	4.05	152	646		2560	6	4	0	

TABLE V

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What Is Claimed Is:

1. A monolithic catalytic structure comprising a catalytically active base metal oxide of the perovskite, spinel, corundum or ilmenite crystal structure suitable for forming structurally sound catalytic compositions.

5

2. A catalytic structure as in Claim 1 in which the active metal oxide is of the perovskite crystal structure  $ABO_3$  in intimate admixture with an additional base metal oxide of the perovskite crystal structure  $ABO_3$  suitable for forming structurally sound catalytic compositions.

10

3. A catalytic structure as in Claim 2 in which the active metal oxide is comprised of a metal of the cation B selected from the group consisting of Cr, Ni, Mn, Fe, Sr, and Ca.

15

4. A catalytic structure as in Claim 2 in which the additional metal oxide is comprised of a metal of the cation A selected from the group consisting of La and Sr and is further comprised of a metal of the cation B selected from the group consisting of Al and Cr.

20

5. A catalytic structure as in Claim 1 in which the active metal oxide is of the spinel crystal structure  $A[B_2]O_4$  or  $B[AB]O_4$  in intimate admixture with an additional base metal oxide of the spinel crystal structure suitable for forming structurally sound catalytic compositions.

25

6. A catalytic structure as in Claim 5 in which the active metal oxide is comprised of a metal of the cation B selected from the group consisting of Ni, Fe and Cr.

30

7. A catalytic structure as in Claim 5 in which the active metal oxide comprises  $Fe_3O_4$  or  $NiAl_2O_4$  and the additional metal oxide comprises  $MgAl_2O_4$ .

35

8. A catalytic structure as in Claim 5 in which the active metal oxide comprises  $Fe_3O_4$  with Cr.

9. A catalytic structure as in Claim 1 in which the active metal oxide is of the corundum crystal structure  $B_2O_3$  or of the ilmenite crystal structure  $ABO_3$  in



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intimate admixture with an additional base metal oxide of the corundum crystal structure suitable for formation of a structurally sound catalytic composition.

- 5 10. A catalytic structure as in Claim 9 in which the active metal oxide of the corundum structure is comprised of a metal of the cation B selected from the group consisting of Cr, Co and Fe.
- 10 11. A catalytic structure as in Claim 9 in which the active metal oxide of the ilmenite structure is comprised of a metal selected from the group consisting of Fe and Cr.
12. A catalytic structure as in Claims 10 or 11 in which the additional metal oxide is comprised of the metal Al of the cation B.
- 15 13. A catalytic structure as in Claim 9 in which the active metal oxide comprises yttria-stabilized  $\text{Co}_2\text{O}_3$ .
- 20 14. A combustion process comprising combusting reactants in the presense of a monolithic catalytic structure comprising a catalytically active base metal oxide of the perovskite, spinel, corundum or ilmenite crystal structure suitable for forming structurally sound catalytic compositions.
- 25 15. A combustion process as in Claim 14 in which the active metal oxide is of the perovskite crustal structure  $\text{ABO}_3$  in intimate admixture with an additional base metal oxide of the perovskite crustal structure  $\text{ABO}_3$  suitable for forming structually sound catalytic compositions.
- 30 16. A combustion process as in Claim 15 in which the active metal oxide is comprised of a metal of the cation B selected from the group consisting of Cr, Ni, Mn, Fe, Sr, and Ca.
- 35 17. A combustion process as in Claim 15 in which the additional metal oxide is comprised of a metal of the cation A selected from the group consisting of La and Sr and is further comprised of a metal of the cation B selected from the group consisting of Al and Cr.

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18. A combustion process as in Claim 14 in which the active metal oxide is of the spinel crystal structure  $A[B_2]O_4$  or  $B[AB]O_4$  in intimate admixture with an additional base metal oxide of the spinel crystal structure suitable for forming structurally sound catalytic compositions.

5

19. A combustion process as in Claim 18 in which the active metal oxide is comprised of a metal of the cation B selected from the group consisting of Ni, Fe and Cr.

10

20. A combustion process as in Claim 18 in which the active metal oxide comprises  $Fe_3O_4$  or  $NiAl_2O_4$  and the additional metal oxide comprises  $MgAl_2O_4$ .

15

21. A combustion process as in Claim 18 in which the active metal oxide comprises  $Fe_3O_4$  with Cr.

20

22. A combustion process as in Claim 14 in which the active metal oxide is of the corundum crystal structure  $B_2O_3$  or of the ilmenite crystal structure  $ABO_3$  in intimate admixture with an additional base metal oxide of the corundum crystal structure suitable for formation of a structurally sound catalytic composition.

25

23. A combustion process as in Claim 22 in which the active metal oxide of the corundum structure is comprised of a metal of the cation B selected from the group consisting of Cr, Co and Fe.

30

24. A combustion process as in Claim 22 in which the active metal oxide of the ilmenite structure is comprised of a metal selected from the group consisting of Fe and Cr.

35

25. A combustion process as in Claims 23 or 24 in which the additional metal oxide is comprised of the metal Al of the cation B.

26. A combustion process as in Claim 22 in which the active metal oxide comprises yttria-stabilized  $Co_2O_3$ .

27. A method of formulating a catalyst system comprising the steps of



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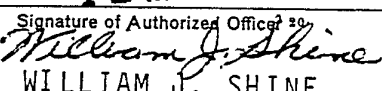
preparing an intimate admixture of a catalytically active base metal oxide having the perovskite crystal structure and an average particle size on the order of 10-20 microns with an additional base metal oxide having the perovskite crystal structure of the type suitable for formation of structurally sound catalytic compositions and with an average particle size on the order of 10-20 microns, forming the mixture into a unitary structure, and calcining the formed structure.

28. A method of formulating a catalyst system comprising the steps of preparing an intimate admixture of a catalytically active base metal oxide of the spinel crystal structure and an average particle size on the order of 10-20 microns with an additional base metal oxide of the spinel crystal structure of the type suitable for formation of structurally sound catalytic compositions and with an average particle size on the order of 10-20 microns, forming the mixture into a unitary structure, and calcining the formed structure.

29. A method of formulating a catalyst structure comprising the steps of preparing an intimate admixture of a catalytically active base metal oxide of the corundum crystal structure or of the ilmenite crystal structure, said active metal oxides having an average particle size on the order of 10-20 microns, with an additional base metal oxide of the corundum crystal structure of the type suitable for formation of structurally sound catalytic compositions and having an average particle size on the order of 10-20 microns, forming the mixture into a unitary structure, and calcining the formed structure.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 79/00813

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. <sup>3</sup> B01J 35/04; F23 D/1700		
US. CL. 252/477R; 431/7		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
US	252/462 156/89 422/177 423/213.5	
	252/477R 264/44 422/180 428/116	
	106/44 264/59 423/213.2 431/7	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>*</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X	US, A, 3,755,204, Published, 28 August 1973, Sergeys, See Example 11	1,14
X	US, A, 4,134,852, Published, 16 January 1979, Volin, See Column 11, Lines 13-16	1,14
A	US, A, 3,870,455, Published, 11 March 1975, Hindin	1-29
A	US, A, 3,974,255, Published, 10 August 1976, Erickson et al	1-29
A	US, A, 3,904,553, Published, 09 September 1975, Campbell et al	1-29
A	US, A, 4,126,580, Published, 21 November 1978, Lauder	1-29
A	US, A, 4,151,123, Published, 24 April 1979, McCann	1-29
<p><sup>*</sup> Special categories of cited documents: <sup>16</sup></p> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> </div> <div style="width: 45%;"> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>2</sup>	Date of Mailing of this International Search Report <sup>2</sup>	
18 APRIL 1980	12 MAY 1980	
International Searching Authority <sup>1</sup>	Signature of Authorized Officer <sup>20</sup>	
ISA/US	 WILLIAM J. SHINE	