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(54) **CONVERSION OF NITROGEN OXIDES IN THE PRESENCE OF A CATALYST SUPPORTED ON A MESH-LIKE STRUCTURE**

(75) Inventors: **Joakim A. Carlborg**, Växjö (SE); **Yun-Feng Chang**, Randolph, NJ (US); **Lawrence L. Murrell**, South Plainfield, NJ (US); **Robert E. Trubac**, Ridgewood, NJ (US); **Rudolf A. Overbeek**, Chatham Township, NJ (US); **Verena R. Schmidt**, Zurich (CH); **Chuen Y. Yeh**, Edison, NJ (US); **Lothar Schuh**, Plankstadt (DE)

(73) Assignee: **ABB Lummus Global, Inc.**, Bloomfield, NJ (US)

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(Under 37 CFR 1.47)

Related U.S. Application Data

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(60) Provisional application No. 60/222,261, filed on Jul. 31, 2000, and provisional application No. 60/159,800, filed on Oct. 15, 1999.

(51) Int. Cl.^{7} **B01J 8/00; C01B 21/00**
(52) U.S. Cl. **423/239.1**; 423/213.2
(58) Field of Search 423/213.2, 239.1

(56) **References Cited**

U.S. PATENT DOCUMENTS

14,302 A * 8/1856 Busshe et al. 423/239.1

(Continued)

FOREIGN PATENT DOCUMENTS

DE 3923094 A1 1/1991

(Continued)

OTHER PUBLICATIONS

Christopher J. Marrion et al, *Composite fiber structures for catalysts and electrodes*, Journal of Power Sources, 47 (1994) 297–302.

Primary Examiner—Stanley S. Silverman
Assistant Examiner—Jonas N. Strickland
(74) *Attorney, Agent, or Firm*—Carella, Byrne, Bain, Gilfillan, Cecchi et al.; Elliot M. Olstein; William Squire

(57) **ABSTRACT**

An apparatus for converting at least one nitrogen oxide, such as NO, O_2, or N_2O converts oxide in the presence of a catalyst supported on a metal mesh-like structure. The mesh-like structure is preferably fibrous formed of metal or ceramic fibers which may include knitted wire, sintered metal fibers and so on and has a porosity greater than about 85%. The mesh is formed into channels, preferably corrugations, and includes vortex generators, which generate turbulence to create a pressure differential across the mesh, to promote flow of fluids through the mesh pores which normally do not exhibit flow therethrough in the absence of such pressure differential. Preferred embodiments of structured packing and monoliths are disclosed each having a catalyst preferably in the mesh pores and/or coated on the fibers for converting the nitrogen oxide. In one embodiment, corrugated mesh-like sheets are arranged in series with a ceramic solid monolith structure with the corrugated sheets initially receiving the fluid with the at least one nitrogen oxide to be converted and which fluid then flows into the monolith structure to complete the conversion. In other embodiments, the mesh-like structure may have different configurations including a honeycomb arrangement and may include metal, metal and ceramic or ceramic and may be fibrous.

9 Claims, 16 Drawing Sheets
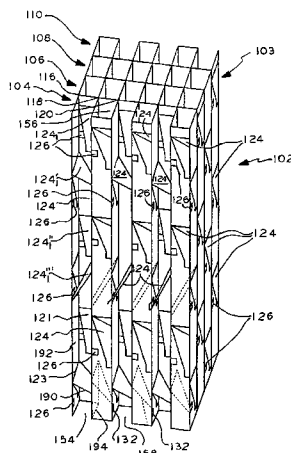
U.S. PATENT DOCUMENTS

2,627,531 A		2/1953	Vogt
4,027,476 A		6/1977	Schmidt
4,038,214 A		7/1977	Gotoh et al.
4,113,660 A		9/1978	Abe et al.
4,280,926 A		7/1981	Abe et al.
4,399,185 A		8/1983	Petrow
4,416,800 A		11/1983	Abe et al.
4,446,250 A		5/1984	Niwa et al.
4,464,482 A		8/1984	Bird et al.
4,520,124 A		5/1985	Abe et al.
4,608,361 A		8/1986	Kanamori et al.
4,762,956 A		8/1988	Liu et al.
4,902,418 A		2/1990	Ziegler
4,921,641 A		5/1990	Lavin
4,939,113 A		7/1990	Tauster et al.
4,965,243 A		10/1990	Yamada et al.
5,080,963 A		1/1992	Tatarchuk et al.
5,096,663 A		3/1992	Tatarchuk
5,102,745 A		4/1992	Tatarchuk et al.
5,162,287 A		11/1992	Yoshimoto et al.
5,165,899 A		11/1992	Delaunay et al.
5,179,061 A		1/1993	Haerle
5,235,102 A		8/1993	Palmer et al.
5,304,330 A		4/1994	Tatarchuk et al.
5,425,236 A		6/1995	Haerle
5,476,783 A		12/1995	Mutsakis et al.
5,490,977 A		2/1996	Wan et al.
5,541,147 A		7/1996	Friedlander et al.
5,582,810 A	*	12/1996	Tretjak 423/239.2
5,587,136 A	*	12/1996	Ikeyama et al. 423/239.1
5,651,946 A		7/1997	Dekumbis et al.
5,665,321 A		9/1997	Campbell et al.
H1682 H		10/1997	Brown et al.
5,753,583 A		5/1998	Heineke et al.
5,762,885 A		6/1998	Debbage et al.
5,795,456 A		8/1998	Friedman et al.
5,800,790 A		9/1998	Imamura et al.
5,997,829 A		12/1999	Sekine et al.
5,997,830 A	*	12/1999	Itoh et al. 423/213.5
6,056,928 A	*	5/2000	Fetzer et al. 423/235

FOREIGN PATENT DOCUMENTS

DE	4206812 A1	9/1992
DE	198 05 444	8/1999
EP	0 441 062 A	8/1991
EP	O 574 012	12/1993
EP	0903 476 A1	3/1999
EP	0 903 476	3/1999
RO	258290	9/1995
WO	WO 95/35152	12/1995
WO	WO96/37288	11/1996
WO	WO99/15715	4/1999
WO	WO00/53904	9/2000

* cited by examiner

DIRECTION OF
FLOW

F I G. 1

f

H

8

α

ANGLE OF INCLINATION

2

W

4

L

F I G. 1a

b

6

a

a = CORPUGATION
HEIGHT
b = PITCH LENGTH

F I G . 2

FIG. 3a

NO, NH$_3$

MONOLITH

10

L$_1$

FIG. 3b

NO, NH$_3$

12

MEC

L$_2$
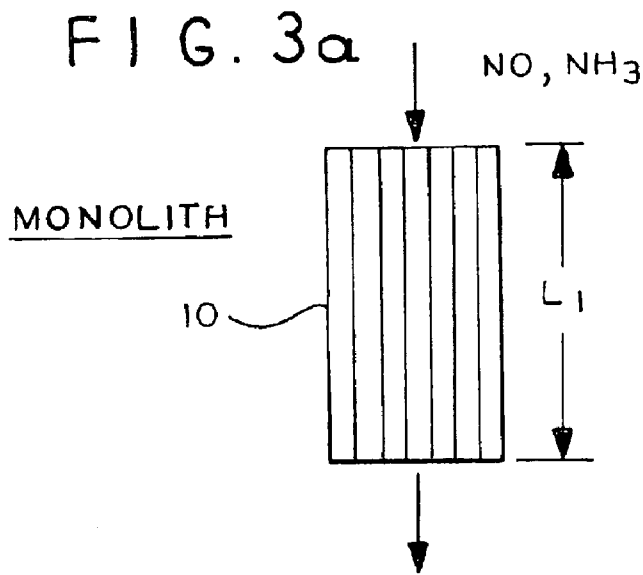
L$_2$<L$_1$

FIG. 3c
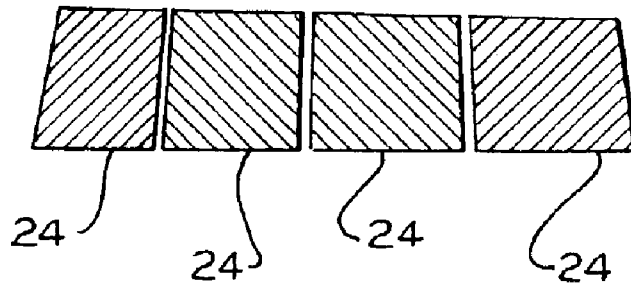
NO, NH$_3$

14

45° MEC

16

L$_3$

L$_2$<L$_3$<L$_1$

MONOLITH
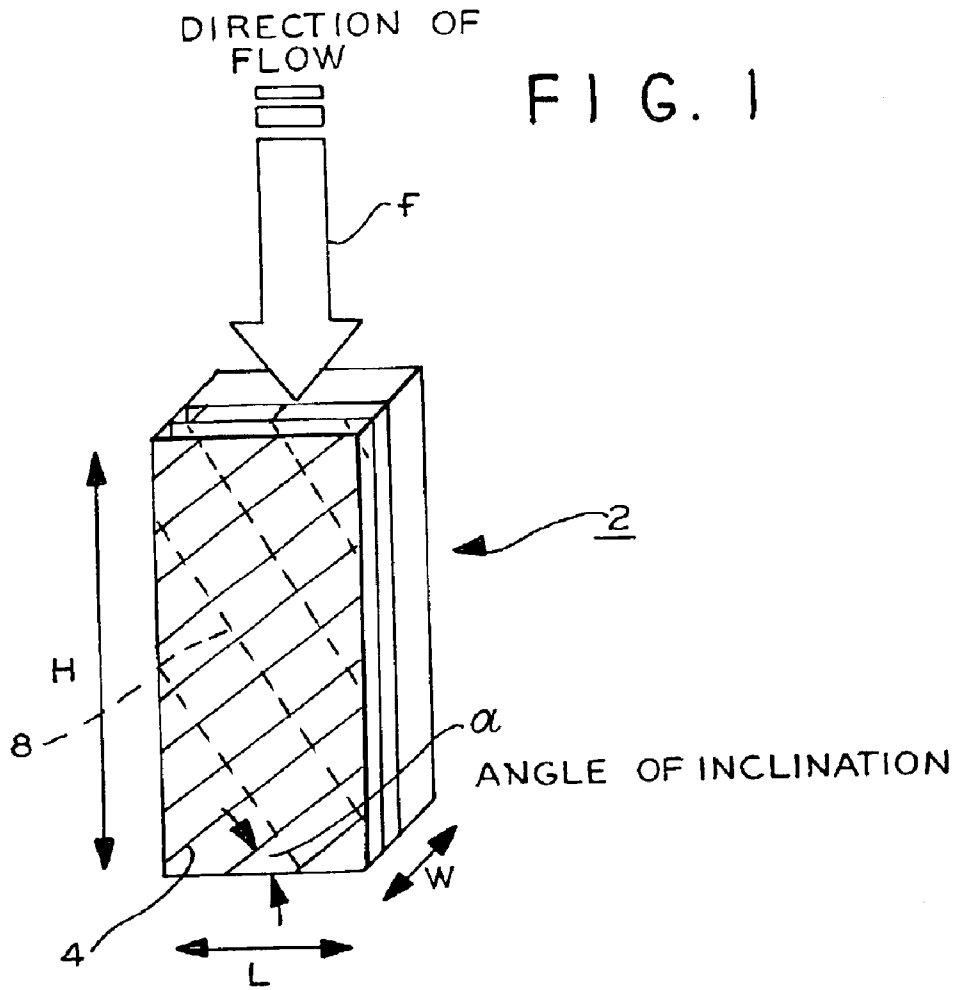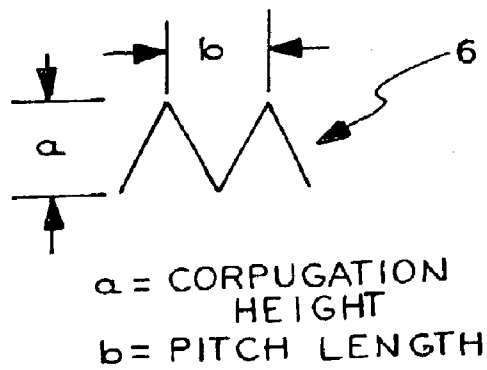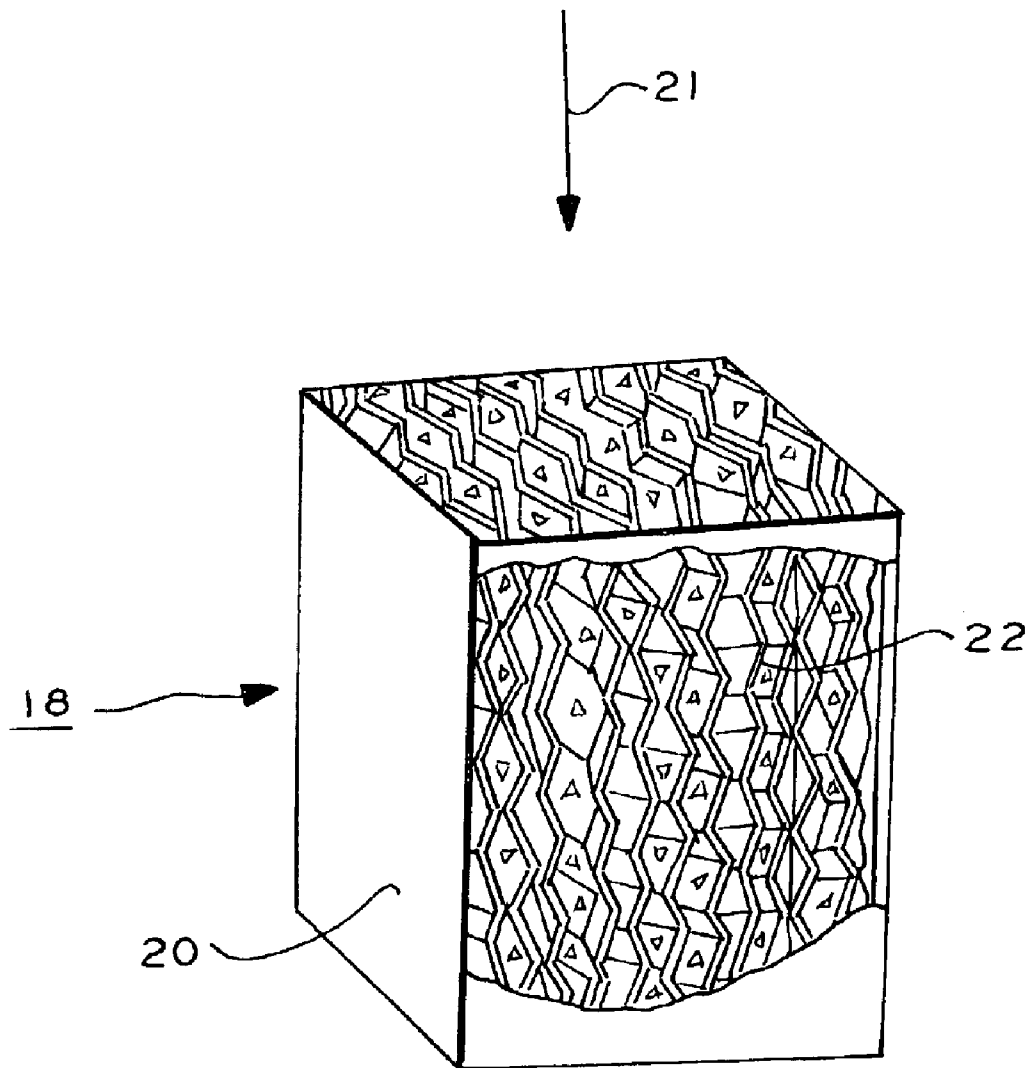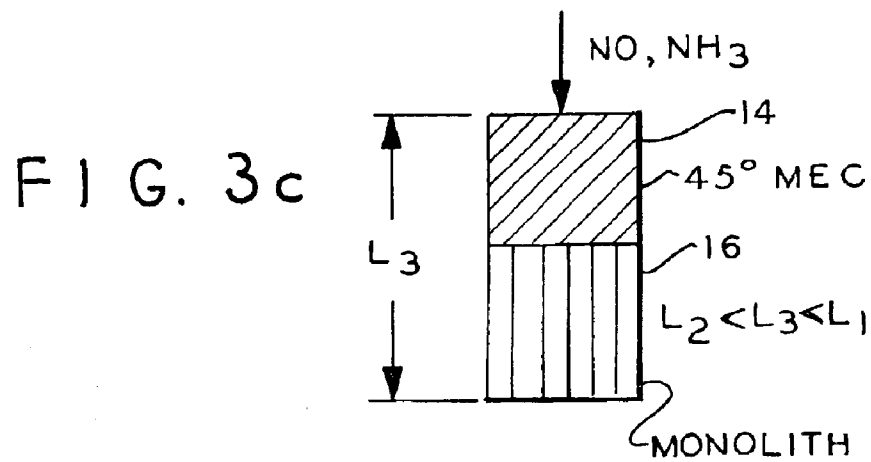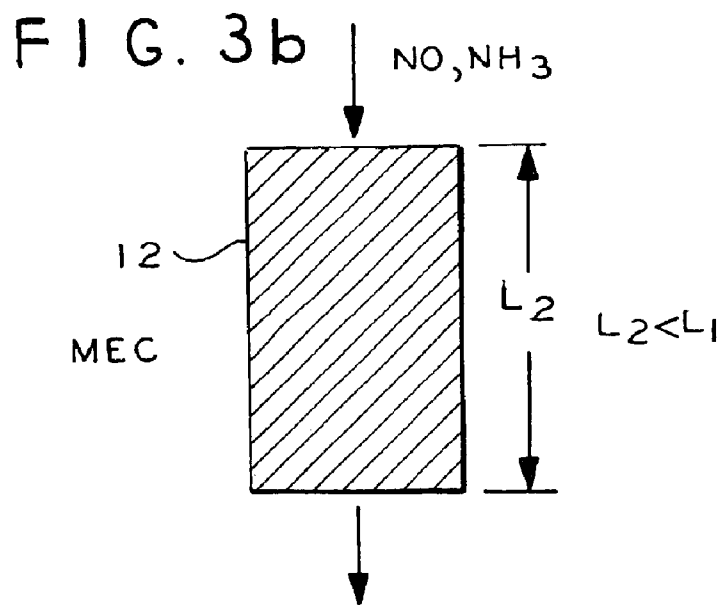
F I G. 4

F I G. 5
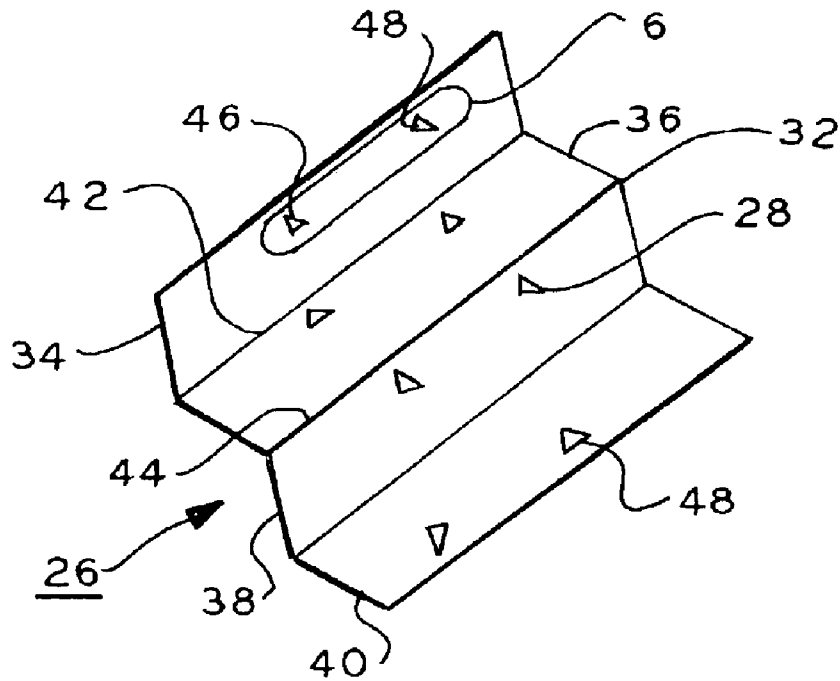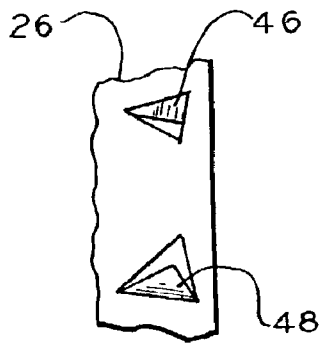
FIG. 6   FIG. 7
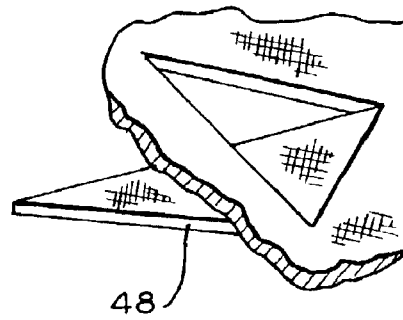
FIG. 8
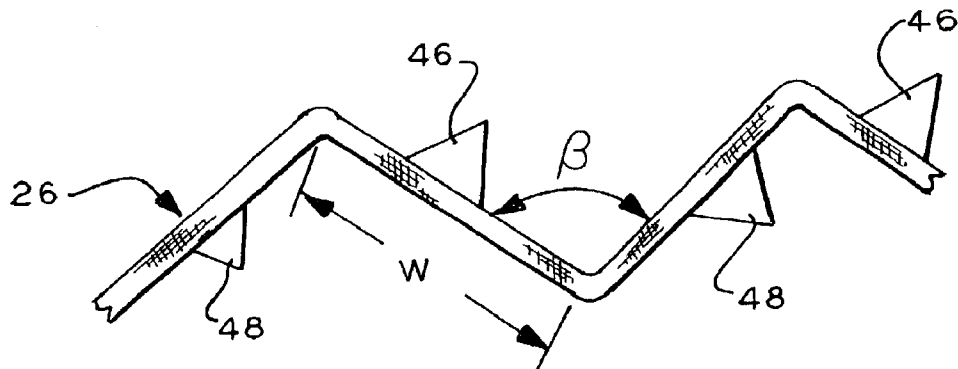
F I G. 9
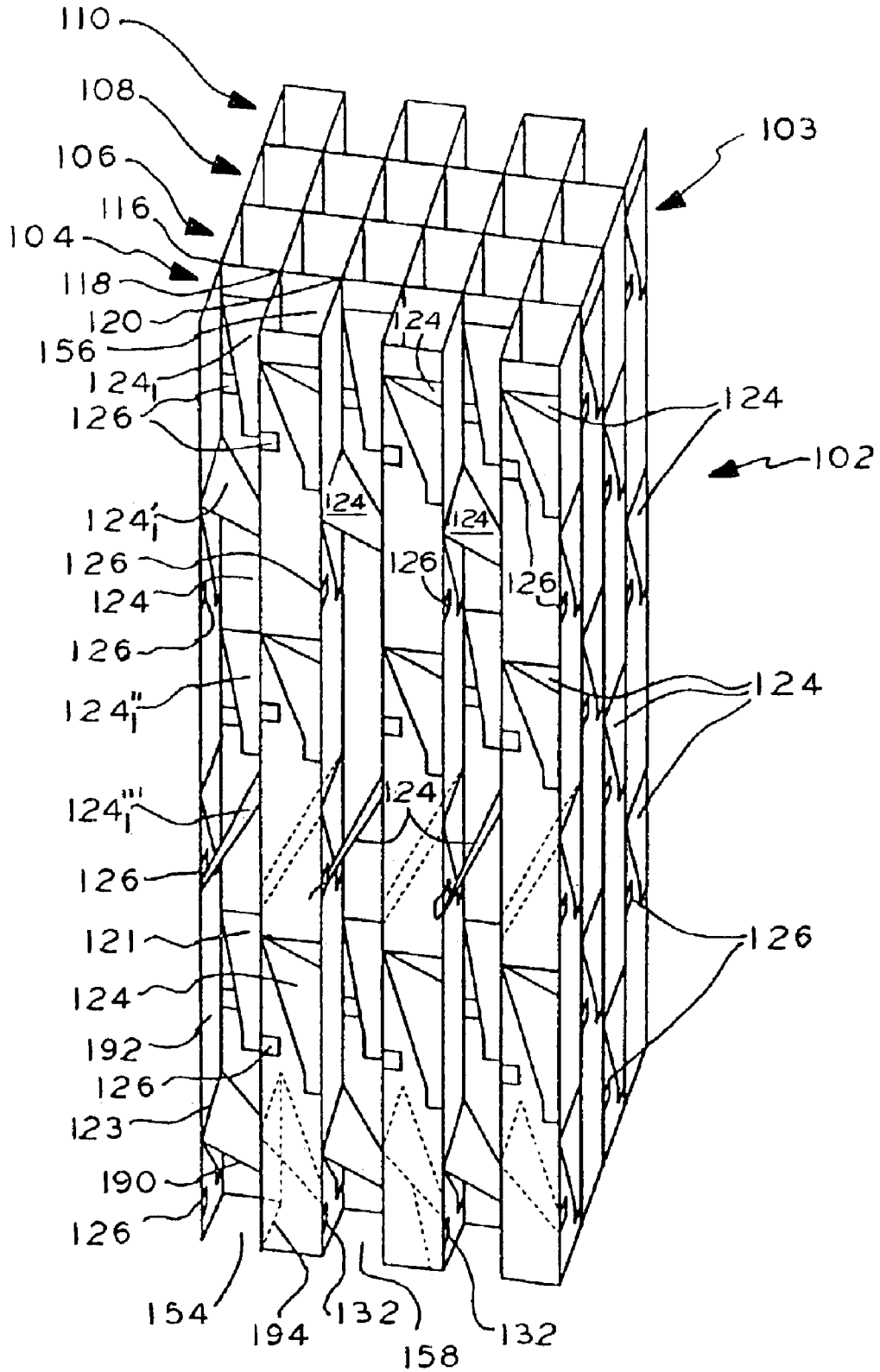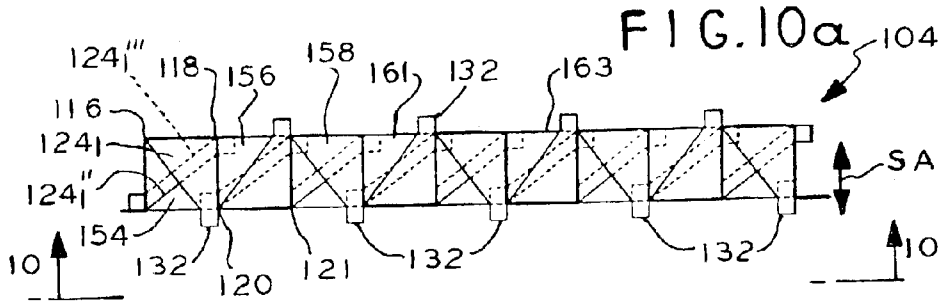
FIG.10a

FIG.10
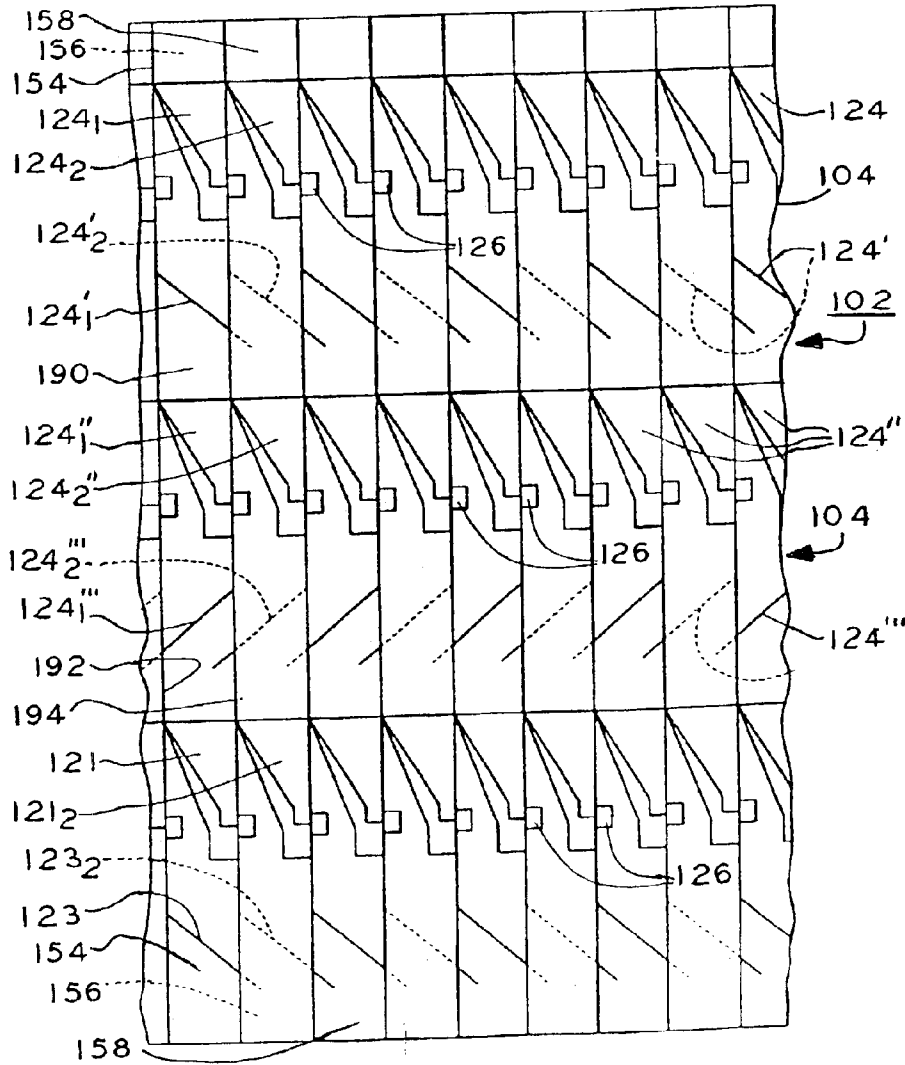
F I G. 11
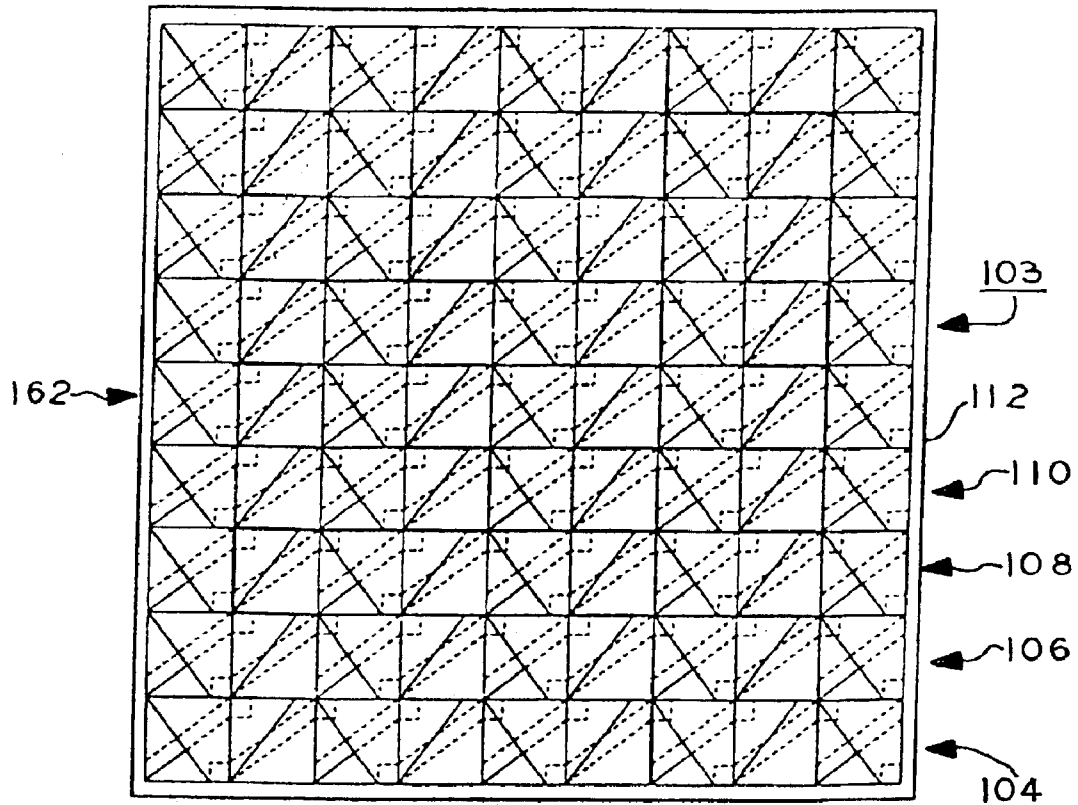
F I G . 1 2
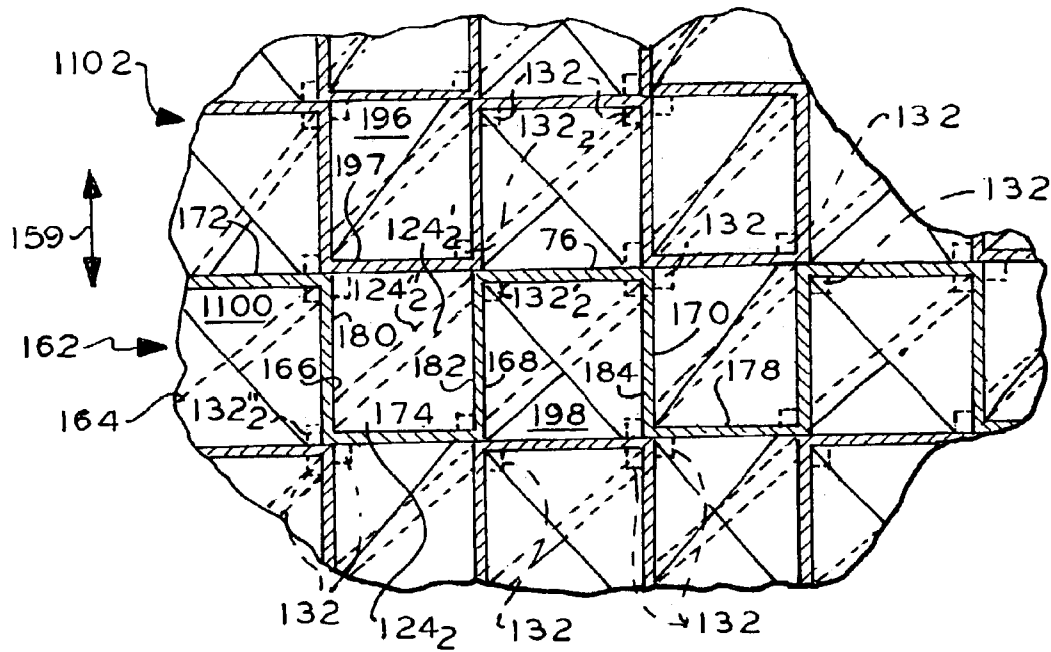
FIG. 13
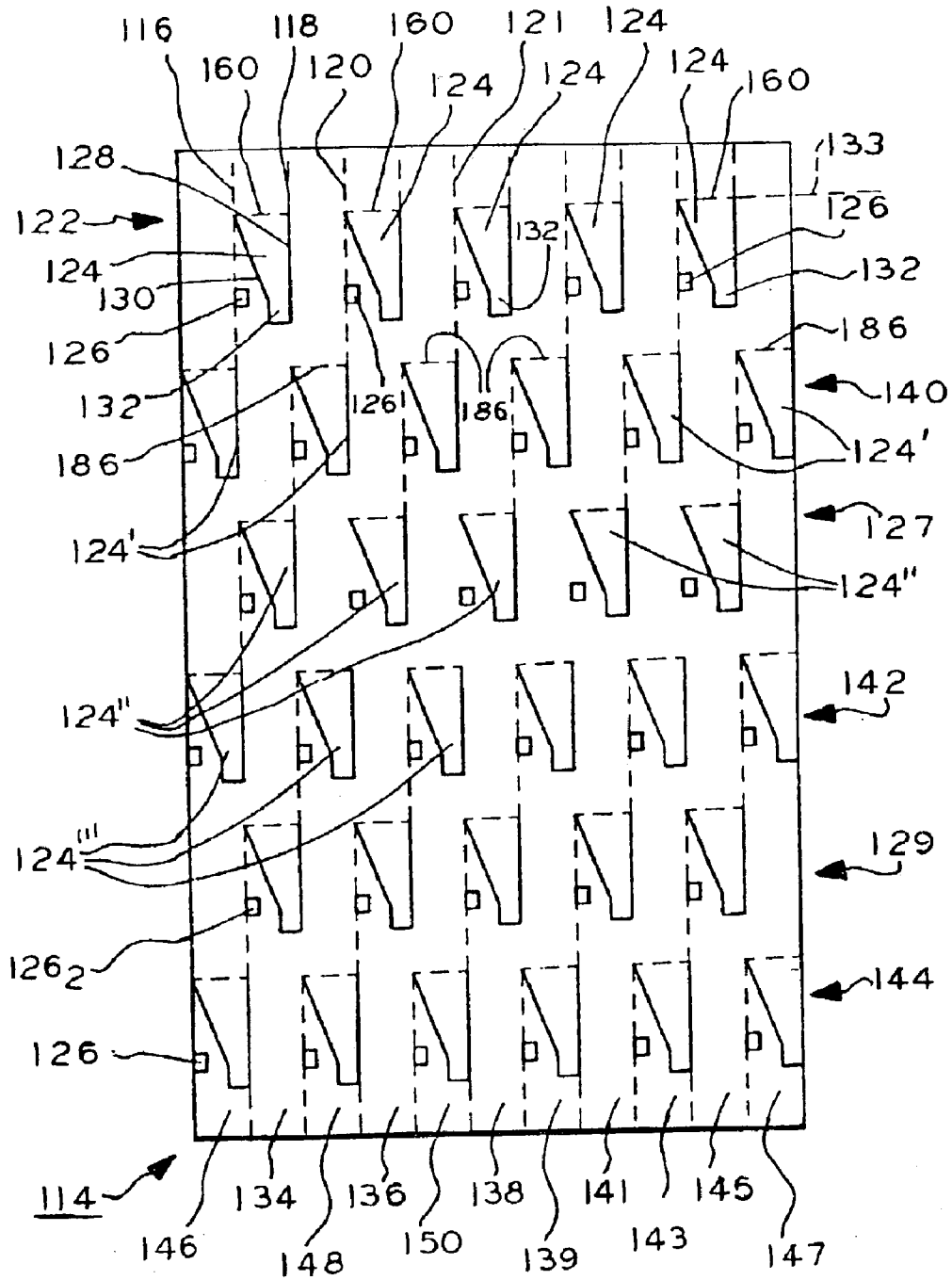
F I G. 14

FIG. 15
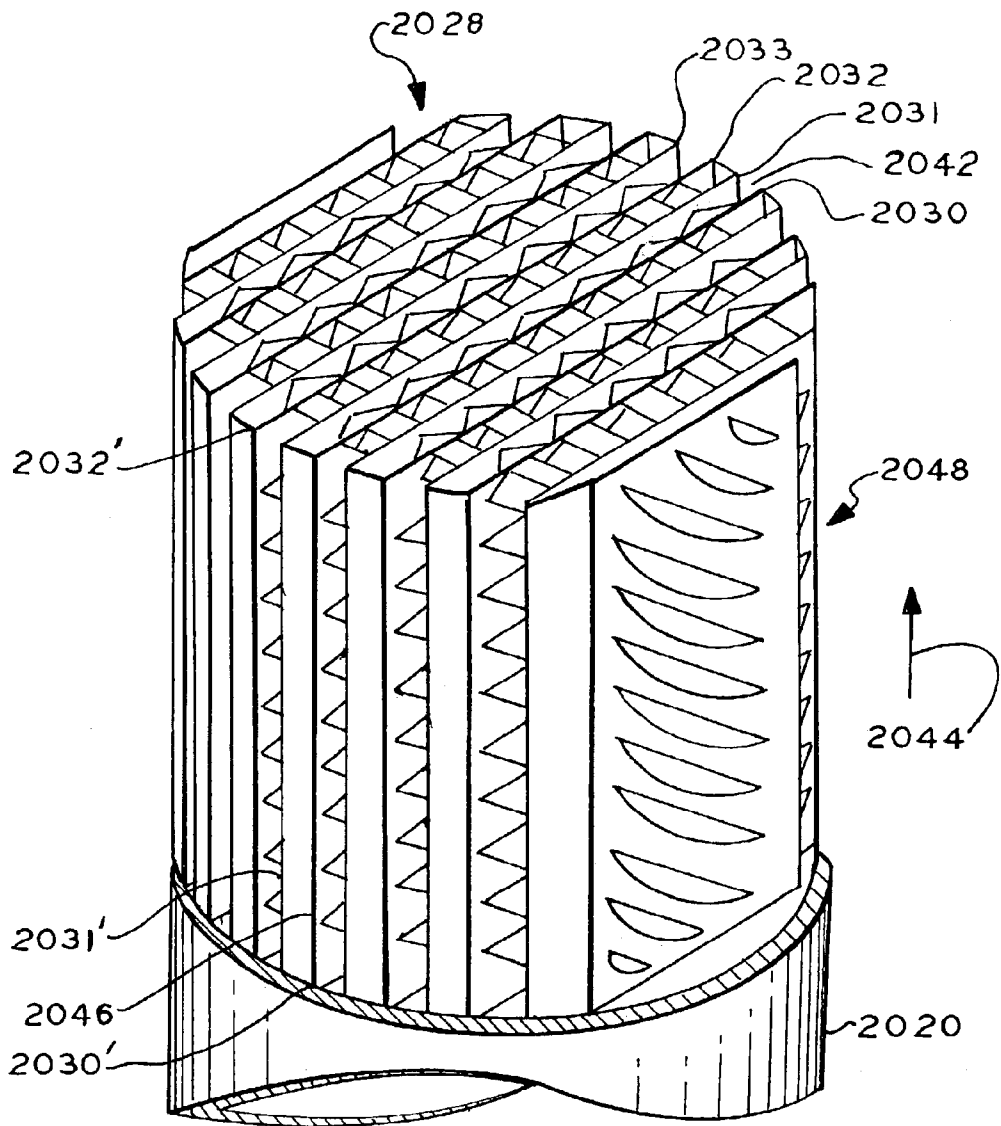
F I G . 16

F I G. 17

FIG. 18

FIG. 19

CONVERSION OF NITROGEN OXIDES IN THE PRESENCE OF A CATALYST SUPPORTED ON A MESH-LIKE STRUCTURE

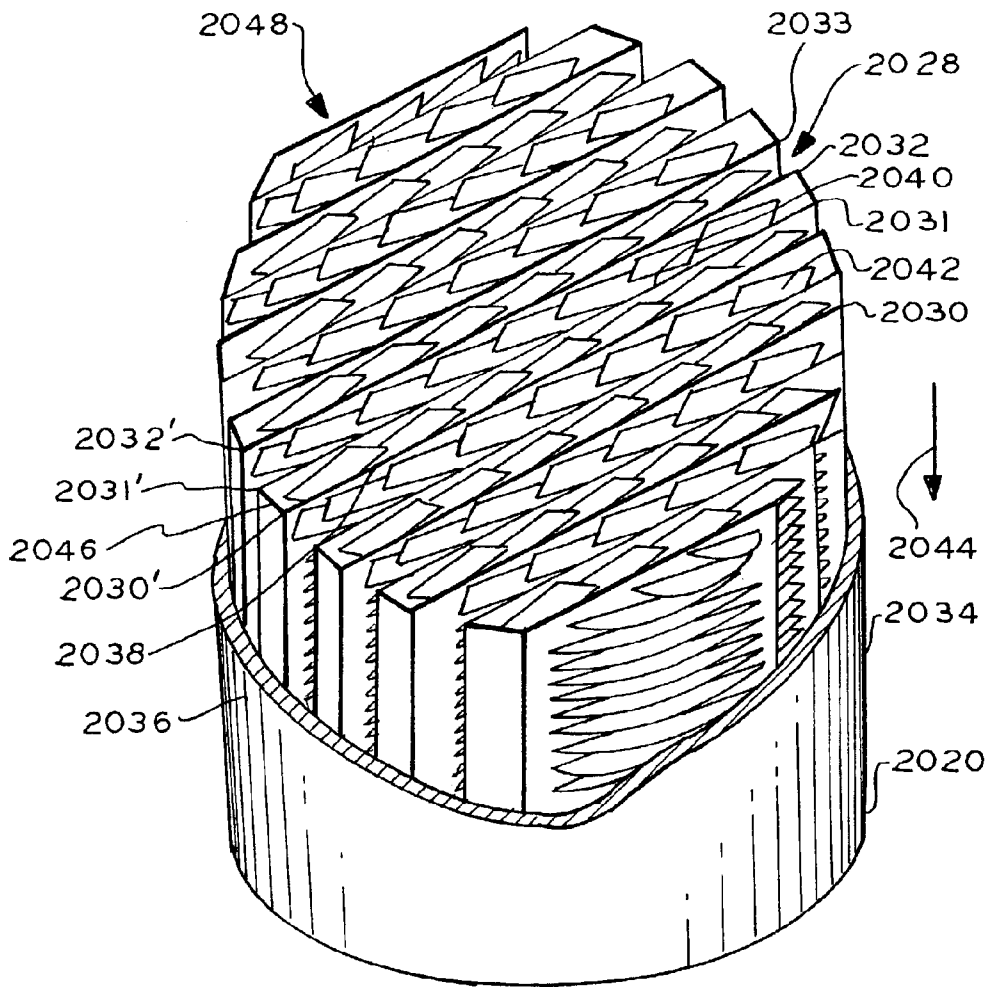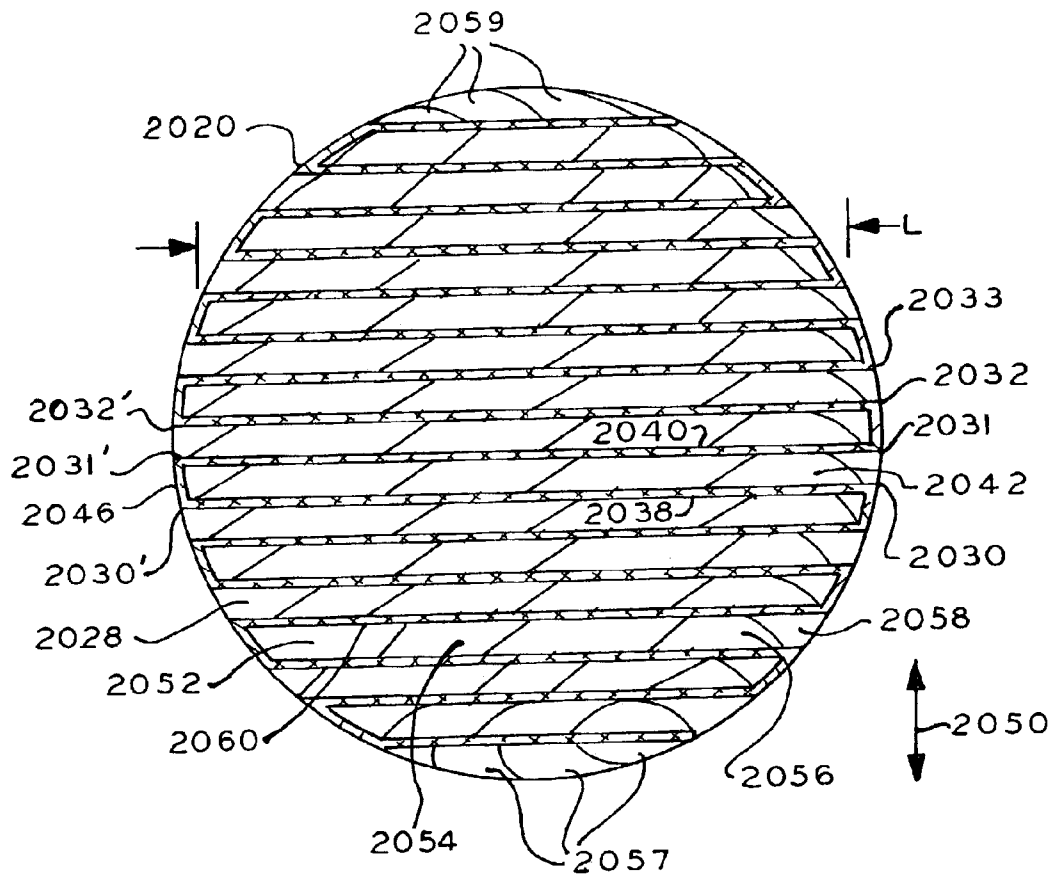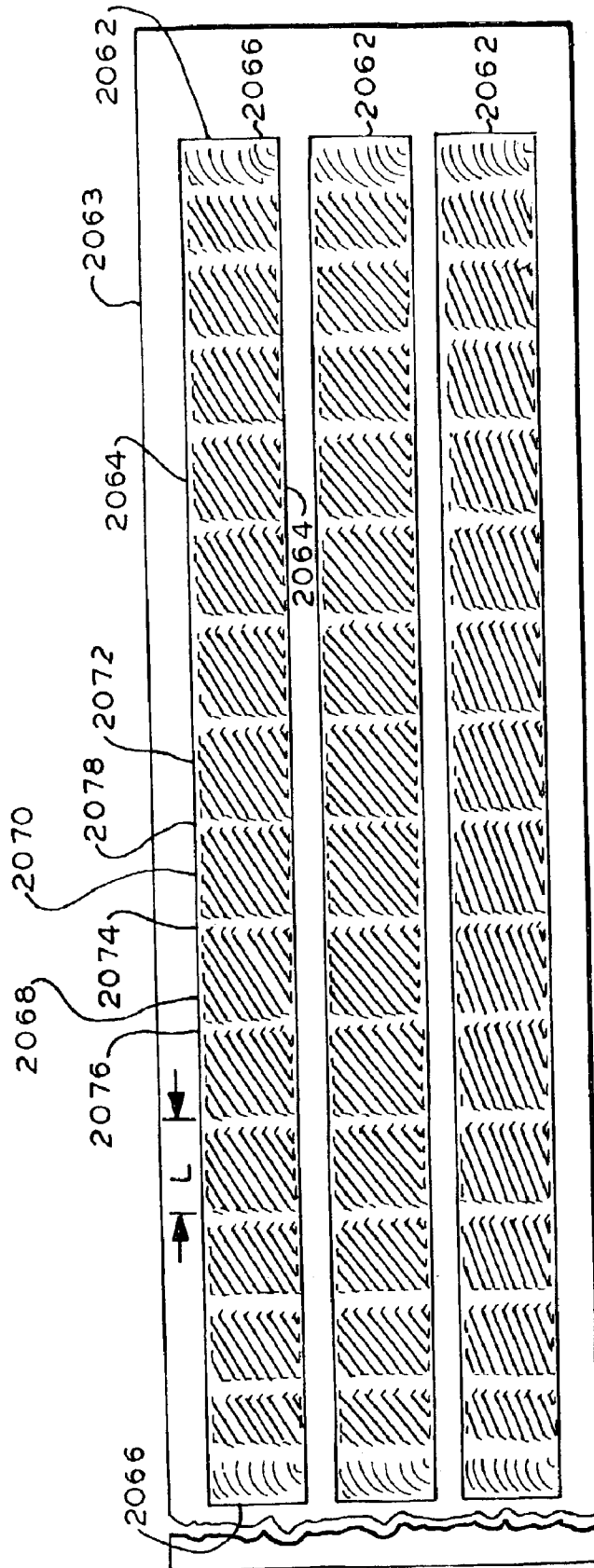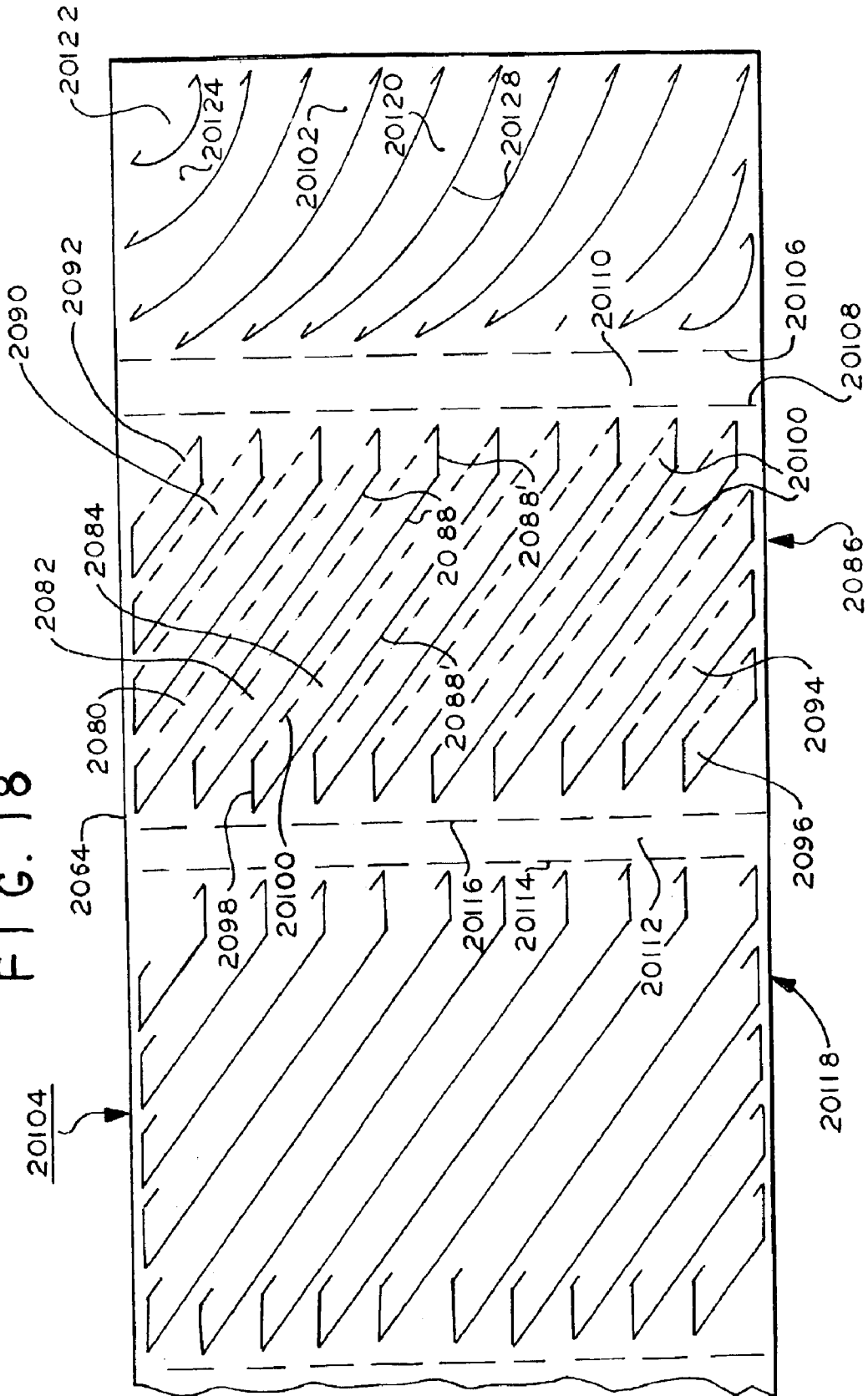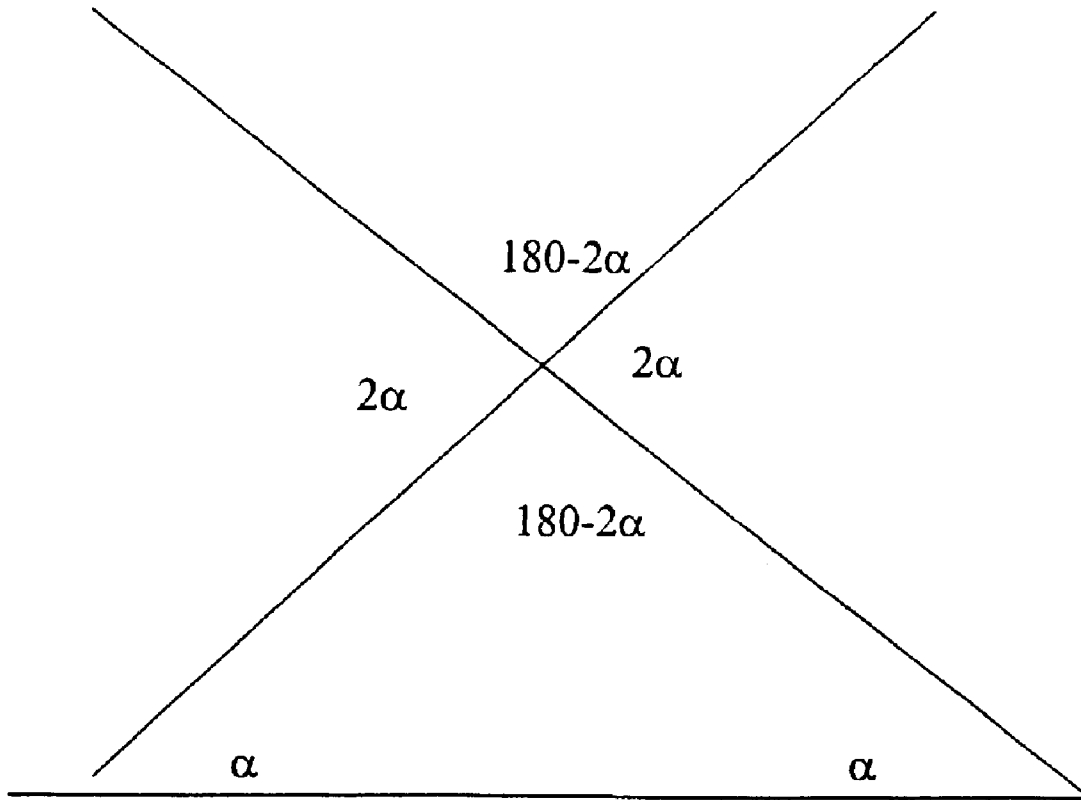This application is a divisional application of Ser. No. 09/687,976, now U.S. Pat. No. 6,534,022, filed Oct. 13, 2000, incorporated by reference in its entirety.

This application claims priority on provisional applications Ser. No. 60/159,800 filed Oct. 15, 1999 and Ser. No. 60/222,261 filed Jul. 31, 2000, both abandoned.

This invention relates to the conversion of nitrogen oxides, such as NO and NO_2, and more particularly, to the conversion of nitrogen oxides in the presence of a catalyst supported on a mesh-like structure.

CROSS REFERENCE TO RELATED APPLICATIONS

Of interest are commonly owned U.S. applications Ser. No. 09/181,186 entitled Method and Apparatus for Making a Catalyst Carrier Device Element filed Oct. 28, 1998 in the name of Vogt et al., now U.S. Pat. No. 6,276,045 and corresponding to PCT/US99/24907 filed Oct. 21, 1999; Ser. No. 09/265,164 entitled Exhaust Gas Catalytic Converter filed Mar. 9, 1999 in the name of J. Lloyd et al. abandoned and corresponding to PCT/US00/06137 filed Mar. 8, 2000; Ser. No. 09/156,023 entitled Coated Products filed Sep. 17, 1998 in the name of L. Schuh et al., now U.S. Pat. No. 6,217,732 and corresponding to PCT/US98/19811 filed Sep. 23, 1998; Ser. No. 09/589,817 entitled Heat Exchanger/ Reactor Apparatus filed Jun. 7, 2000 in the name of Timothy Griffin et al., abandoned, Ser. No. 09/322,524 entitled Structured Packing and Element Therefor filed May 28, 1999 in the name of Rudolf A. Overbeek et al., abandoned, and corresponding to PCT/US99/10784 filed May 14, 1999; Ser. No. 09/002,539 entitled Structured Packing and Element Therefor filed Jan. 2, 1998 in the name of Bettina Paikert et al., now U.S. Pat. No. 6,277,340, corresponding to PCT/ US98/27699 filed Dec. 29, 1998 all of the above US patents incorporated by reference herein in their entirety.

Nitrogen oxides, such as NO and NO_2, are undesired by-products found in exhaust gases in various plants such as power plants, including natural gas-fired power plants, waste-to-energy plants, and fuel combustion plants. Nitrogen oxides also may be found in the combustion products of diesel engines.

U.S. Pat. No. 4,280,926 discloses a method for producing a catalytic material for reduction of nitrogen oxides utilizing ammonia as reducing agent. The support material has the shape of a fibrous sheet consisting of non-metallic inorganic fibers mixed with a catalytic active powder. The product can be further treated by impregnation in catalytically active agents. The sheets can be shaped to a honeycomb structure and fixated by a silica solution adhesive.

U.S. Pat. No. 4,416,800 discloses a method for producing a catalytic material. The support material has the shape of a fibrous sheet consisting of non-metallic inorganic fibers mixed with a catalyst carrier powder. The product can be further treated by impregnation in slurry or solution containing carrier materials and catalytically active agents. The catalytic material can be used for:

a) reduction of nitrogen oxides in the presence of ammonia (catalyst: Cu, Fe, V, W and Mo on Al_2O_3 or TiO_2)

b) oxidation of carbon monoxide and hydrocarbons (catalyst: Pt on Al_2O_3 or TiO_2)

In accordance with an aspect of the present invention, there is provided a process for removing at least one nitrogen

oxide from a fluid, in particular a gas. The process comprises converting the at least one nitrogen oxide in the presence of a catalyst supported on a mesh-like structure. The mesh-like structure preferably has a porosity of greater than about 85%. Preferably the mesh-like structure is fibrous and made of a metal, metal and ceramic or a ceramic.

In a further aspect the mesh-like structure has a porosity of greater than 90%.

In a still further aspect, the at least one nitrogen oxide is selected from the group consisting of NO and NO_2 and N_2O.

In a further aspect, the at least one nitrogen oxide is selected from the group consisting of NO and NO_2 or mixtures thereof. In another aspect, the at least one nitrogen oxide is NO. In another aspect, the at least one nitrogen oxide is NO_2. In another embodiment, the at least one nitrogen oxide is N_2O. In yet another aspect, the at least one nitrogen oxide includes NO and NO_2. In yet another aspect, the at least one nitrogen oxide includes NO, NO_2 and N_2O.

In a further aspect, the catalyst is coated on the mesh-like structure and preferably the coating thickness is less than 30 microns.

In a still further aspect, a process for removing NO from a gas comprises oxidizing the contained NO to NO_2 and contacting the NO_2 with a metal carbonate, bicarbonate or hydroxide supported on a mesh-like structure, the mesh-like structure comprising a fibrous material of at least one of a metal, metal and ceramic or ceramic and having a porosity of at least 87%.

IN THE DRAWING

FIG. 1 is an isometric diagrammatic view of a packing structure useful for explaining the principles of the present invention;

FIG. 1a is a diagram useful for explaining parameters of a corrugated packing material.

FIG. 2 is an isometric fragmented sectional view of view of a packing structure embodiment for use with the present invention;

FIGS. 3a, 3b and 3c are diagrammatic view of different combinations of packing elements showing dimensional relationship between the different combinations to obtain a given catalytic result;

FIG. 4 is a perspective view of a plurality of corrugated packing elements of FIG. 2 laid out in side-by-side relation to show their relative corrugation orientations in the embodiment of FIG. 2;

FIG. 5 is a more detailed perspective view of a portion of one of the corrugated elements used in the embodiment of FIGS. 2 and 4;

FIG. 6 is a more detailed view of a portion of the element of FIG. 5 taken at region 6;

FIG. 7 is a more detailed view one of the vortex generators of FIG. 6 taken at region 7;

FIG. 8 is an end view of a portion of the packing element of FIG. 5;

FIG. 9 is an isometric view of a second packing structure embodiment for use with the present invention;

FIG. 10a is a top plan view of one of the packing elements of FIG. 9;

FIG. 10 is a front elevation view of the packing element of FIG. 10a taken along lines 10—10;

FIG. 11 is a top plan view of the structure of FIG. 9;

FIG. 12 is a more detailed view of a portion of the structure of FIG. 11;

FIG. **13** is a front elevation view of a blank forming a packing element of the structure of FIG. **9**;

FIG. **14** is an isometric view of a packing module in accordance with a further embodiment;

FIG. **15** is a further isometric view of the packing module of FIG. **14**;

FIG. **16** is a top plan sectional view of the embodiment of FIG. **14** showing a packing module in a tube;

FIG. **17** is a plan view of a set of blanks used to make the modules of FIGS. **14** and **15**;

FIG. **18** is a more detailed view of a portion of one of the blanks of FIG. **17** illustrating the vane formation; and

FIG. **19** is a diagram useful for explaining certain principles of the present invention.

The term "removing at least one nitrogen oxide," as used herein, means that the at least one nitrogen oxide is reacted with a molecule(s) to produce diatomic nitrogen. Such reactions include, but are not limited to, oxidation-reduction reactions. In another aspect, the at least one nitrogen oxide is first further oxidized and then reacted with a metal carbonate, bicarbonate or hydroxide to produce a metal nitrite and metal nitrate, with the nitrite and nitrate being reduced to produce diatomic nitrogen and regenerate the metal carbonate, bicarbonate or hydroxide.

The mesh-like material is comprised of fibers or wires, such as a wire or fiber mesh, a ceramic fiber mesh, a combination of metal and ceramic fibers, a metal felt or gauze, metal fiber filter or the like. The mesh-like structure may be comprised of a single layer, or may include more than one layer, it may be made of wires; e.g., a knitted wire structure or a woven wire structure and preferably is comprised of a plurality of layers of wires or fibers to form a three-dimensional network of materials. In a preferred embodiment, the support structure is comprised of a plurality of layers of fibers that are oriented randomly in the layers. One or more metals may be used in producing a metal mesh. Alternatively the mesh fibers may include ceramic fibers in place of or in combination with metal fibers. Ceramic fiber meshes are commercially available from Crane & Co. of Massachusetts, USA.

In a preferred embodiment wherein the mesh-like structure is comprised of a plurality of layers of fibers to form the three-dimensional network of materials, the thickness of such support is at least five microns, and generally does not exceed ten millimeters. In accordance with a preferred embodiment, the thickness of the network is, at least 50 microns and more preferably at least 100 microns and generally does not exceed 2 millimeters.

In general, the thickness or diameter of the fibers which form the plurality of layers of fibers is less than about 500 microns, preferably less than about 150 microns and more preferably less than about 30 microns. In a preferred embodiment, the thickness or diameter of the fibers is from about 8 to about 25 microns.

The three dimensional mesh-like structure may be produced as described in U.S. Pat. No. 5,304,330, 5,080,962; 5,102,745 or 5,096,663 incorporated by reference in their entirety. It is to be understood, however, that such mesh-like structure may be formed by procedures other than as described in the aforementioned patents.

The mesh-like structure that is employed in the present invention (without supported catalyst on the mesh) has a porosity or void volume which is greater than 85%, and preferably is greater than 87% and more preferably is greater than 90%. The term "void volume" as used herein is determined by dividing the volume of the structure which is open by the total volume of the structure (openings and mesh material) and multiplying by 100.

In one embodiment, the catalyst is supported on the mesh-like material without the use of a particulate support.

In another embodiment, the catalyst for converting nitrogen oxide(s) is supported on a particulate support that is supported on the mesh-like material. The term particulate as used herein includes and encompasses spherical particles, elongated particles, fibers, etc. In general, the average particle size of the particulate on which catalyst may be supported does not exceed 200 microns and is typically no greater than 50 microns with the average particle size in the majority of cases not exceeding 20 microns. In general, the average particle size of such particulates is at least 0.002 micron and more generally at least 0.5 microns. When the catalyst supported on the particulate support is coated on the mesh, the average particle size of the catalyst support generally does not exceed 10 microns and, when entrapped in the mesh, generally does not exceed 150 microns.

In an embodiment of the invention, the mesh-like structure, that functions as a support for the catalyst is in the form of a shaped structured packing. This packing can be configured as described below in embodiments given by example to provide for turbulence of the gas phase flowing over the catalyst in the reactor. The mesh-like catalyst support structure may be provided with suitable corrugations in order to provide for increased turbulence as described in more detail hereinafter. Alternatively, the mesh-like structure may include tabs or vortex generators to provide for turbulence, also as shown hereinafter. The presence of turbulence generators enhances mixing in the radial (and longitudinal) direction and also improves access to catalyst either coated on or entrapped in the mesh by providing local pressure differentials across the mesh, and thus creating a driving force for flow. The structured packing can also be in the form of a module such as a roll of one or more sheets that is placed into the tubes of a reactor such that the channels in the module follow the longitudinal direction of the tube. The roll can comprise sheets that are flat, corrugated or wavy or a combination thereof and the sheets can contain fins or holes to promote mixing. The sheets can also be shaped into corrugated strips that are separated from each other by a flat sheet that exactly fit the size of the tube and are held together by welds, wires, a cylindrical flat sheet or combinations thereof. Alternatively, the mesh, with metal, metal and ceramic or ceramic fibers, may be formed into a honeycomb structure with parallel channels. The channels of the honeycomb may include holes and/or turbulence generators to allow for increased mass transfer of the reactants to the catalyst.

It is to be understood that the mesh-like support that supports the catalyst may be employed in a form other than as a structured sheet. For example, the mesh-like support may be formed as rings, particles, ribbons, etc. and employed in a reactor as a packed bed.

The catalyst which is supported on the mesh-like structure may be present on the mesh-like support as a coating on the wires or fibers that form the mesh-like structure and/or may be present and retained in the interstices of the mesh-like structure.

The catalyst may be coated on the mesh-like structure by a variety of techniques, e.g., dipping or spraying. The catalyst particles may be applied to the mesh-like structure by contacting the mesh-like structure with a liquid coating composition (preferably in the form of a coating bath) that

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6

includes the particles dispersed in a liquid under conditions such that the coating composition enters or wicks into the mesh-like structure and forms a porous coating on both the interior and exterior portions of the mesh-like structure.

In a preferred embodiment, the liquid coating composition has a kinematic viscosity of no greater than 175 centistokes and a surface tension of no greater than 300 dynes/cm.

In one embodiment, the catalyst is coated onto the mesh by dip-coating. In a preferred embodiment, the three-dimensional metal mesh-like material is oxidized before coating; e.g., heating in air at a temperature of from 300° C. up to 700° C. In some cases, if the mesh-like material is contaminated with organic material, the mesh-like material is cleaned prior to oxidation; for example, by washing with an organic solvent such as acetone.

The coating bath is preferably a mixed solvent system of organic solvents and water in which the particles are dispersed. The polarity of the solvent system is preferably lower than that of water in order to prevent high solubility of the catalyst and to obtain a good quality slurry for coating. The solvent system may be a mixture of water, amides, esters, and alcohols. The kinematic viscosity of the coating bath is preferably less than 175 centistokes and the surface tension thereof is preferably less than 300 dynes/cm.

In a preferred embodiment of the invention, the mesh-like structure that is coated includes metal wires or fibers or ceramic fibers or metal and ceramic fibers and the metal wires or fibers that are coated are selected or treated in a manner such that the surface tension thereof is higher than 50 dynes/cm, as determined by the method described in "Advances in Chemistry, 43, Contact Angle, Wettability and Adhesion, American Chemical Society, 1964. "

In coating a mesh-like structure that includes metal fibers, the liquid coating composition preferably has a surface tension from about 50 to 300 dynes/cm, and more preferably from about 50 to 150 dynes/cm, as measured by the capillary tube method, as described in T. C. Patton, "Paint Flow and Pigment Dispersion", 2nd Ed., Wiley-Interscience, 1979, p. 223. At the same time, the liquid coating composition has a kinematic viscosity of no greater than 175 centistokes, as measured by a capillary viscometer and described in P. C. Hiemenz, "Principles of colloid and Surface Chemistry", 2nd Ed., Marcel Dekker Inc., 1986, p. 182.

In such an embodiment, the viscosity and surface tension of the liquid-coating composition is coordinated with the surface tension of the metal being coated such that the liquid-coating composition is drawn into the interior of the structure to produce a particulate coating on the mesh-like structure upon drying. The metal to be coated preferably has a surface tension which is greater than 50 dynes/cm and preferably is higher than the surface tension of the liquid coating composition to obtain spontaneous wetting and penetration of the liquid into the interior of the mesh.

In the case where the metal of the structure that is to be coated does not have the desired surface tension, the structure may be heat-treated to produce the desired surface tension.

The liquid coating composition can be prepared without any binders or adhesives for causing adherence of the particulate coating to the structure.

The surface of the structure to be coated may also be chemically or physically modified to increase the attraction between the surface and the particles that form the coating; e.g., heat treatment or chemical modification of the surface.

The solids content of the coating bath generally is from about 2% to about 50%, preferably from about 5% to about 30%.

The bath may also contain additives such as surfactants, dispersants, water soluble polymers, etc. In general, the weight ratio of additives to particles in the coating bath is from 0.0001 to 0.4 and more preferably from 0.001 to 0.1.

The mesh-like material preferably is coated by dipping the mesh-like material into a coating bath one or more times while drying or calcining in between dippings. The temperature of the bath is preferably at room temperature, but has to be sufficiently below the boiling point of the liquid in the bath.

After coating, the mesh-like material that includes a porous coating comprised of a plurality of particles is dried, preferably with the material in a vertical position. The drying is preferably accomplished by contact with a flowing gas (such as air) at a temperature of from 20° C. to 150° C. more preferably from 100° C. to 150° C. After drying, the coated mesh-like material is preferably calcined, for example, at a temperature of from 250° C. to 800° C., preferably 300° C. to 500° C., most preferably at about 400° C. In a preferred embodiment, the temperature and air flow are coordinated in order to produce a drying rate that does not affect adversely the catalyst coating, e.g., cracking, blocking of pores, etc. In many cases, a slower rate of drying is preferred. This slower rate of drying can be accomplished by use of a humidified drying gas. It may also be advantageous to vary the humidity of the drying gas as a function of time.

The thickness of the formed coating may vary. In general, the thickness is at least 1 micron and in general no greater than 100 microns. Typically, the coating thickness is less than 50 microns and more typically does not exceed 30 microns. Applicant has found that coating thickness of less than 30 microns enhances catalyst effectiveness and, therefore, increases volumetric activity.

The interior portion of the mesh material that is coated has a porosity which is sufficient to allow the particles which comprise the coating to penetrate or migrate into the three-dimensional network. Thus, the pore size of the three-dimensional material and the particle size of the particles comprising the coating, in effect, determine the amount and uniformity of the coating that can be deposited in the interior of the network of material and/or the coating thickness in the network. The larger the pore sizes the greater the thickness of the coating which can be uniformly coated in accordance with the invention.

In the case where the particles are in the form of a catalyst precursor, the product, after the deposit of the particles, is treated to convert the catalyst precursor to an active catalyst. In the case where the particles which are deposited in the three-dimensional network of material is a catalyst support, active catalyst or catalyst precursor may then be applied to such support, e.g., by spraying, dipping, or impregnation.

In using a coating bath, the coating slurry in some cases may include additives. These additives change the physical characteristics of the coating slurry, in particular the viscosity and surface tension such that during dipping the slurry penetrates the mesh, and a coating can be obtained with a homogeneous distribution on the interior and exterior of the mesh. Sols not only change the physical properties of the coating slurry, but also act as binders. After the deposition, the article is dried and calcined.

As representative stabilizing agents there may be mentioned: a polymer like polyacrylic acid, acrylamines, organic quaternary ammonium compounds, or other special mixes which are selected based on the particles. Alternatively an organic solvent can be used for the same purpose. Examples

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of such solvents are alcohols or liquid paraffins. Control of the pH of the slurry, for example, by addition of HNO_3 is another method of changing the viscosity and surface tension of the coating slurry.

The catalyst may be coated onto the mesh-like catalyst support by an electrophoretic coating procedure, as described in U.S. application Ser. No. 09/156,023, filed on Sep. 17, 1998, now U.S. Pat. No. 6,217,732. In such a procedure, a wire mesh-like structure is employed as one of the electrodes, and the catalyst of the requisite particle size, is suspended in a coating slurry. A potential is applied across the electrodes, one of which is the mesh-like structure formed from a plurality of layers of fibers, and the mesh-like structure is electrophoretically coated with the catalyst.

As hereinabove indicated, the supported selective oxidation catalyst may be supported on the mesh material by entrapping or retaining the particulate in the interstices of the mesh. For example, in producing a mesh-like structure comprised of a plurality of layers of randomly oriented fibers, the catalyst or a catalyst support may be included in the mix that is used for producing the mesh-like structure whereby the mesh-like structure is produced with the catalyst or catalyst support retained in the interstices of the mesh. For example, such mesh-like structures may be produced as described in the aforementioned patents, and with an appropriate catalyst or catalyst support being added to the mesh that contains the fibers and a binder, such as cellulose. The produced mesh structure includes the catalyst retained in the mesh structure.

These and other embodiments should be apparent to those skilled in the art from the teachings herein.

Although in a preferred embodiment, essentially the entire thickness of the material is coated with the catalyst, it is within the spirit and scope of the invention to coat less than the entire thickness with such particles. It also is possible within the spirit and scope of the present invention to have various coating thicknesses within the three-dimensional structure at the internal interstices of the mesh material.

Catalyst for converting nitrogen oxides are known in the art. Representative examples of such include but are not limited to oxides of vanadium, aluminum, titanium, tungsten and molybdenum. Zeolites may also be used. Examples of the latter include ZSM-5 modified with protons or copper, cobalt, silver, zinc, or platinum cations or their combination. Other examples of catalysts used for converting nitrogen oxides are precious metals such as platinum, rhodium and palladium. It is to be understood, however, that the scope of the present invention is not to be limited to the specific catalysts hereinabove described.

The catalyst is supported on the mesh-like structure in an amount effective to convert nitrogen oxide(s). In general, the catalyst is present in an amount of at least 5%, and preferably at least 10%, with the amount of catalyst generally not exceeding 60% and more generally not exceeding 40%, all by weight, based on mesh and catalyst. In one embodiment where the porosity or void volume of the mesh-like structure prior to adding supported catalyst is greater than 87%, the weight percent of catalyst is from about 5% to about 40%, and when the porosity or void volume is greater than 90%, the weight percent of supported catalyst is from about 5% to about 80%.

In one embodiment, the catalyst which is supported on the mesh-like structure is employed in the reduction of nitrogen oxides with a reducing agent e.g. urea, ammonia, hydrocarbons, etc in the presence of oxygen to produce

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nitrogen and water. Reductants such as ammonia or urea are widely used for NOx abatement from stationary sources but not from, mobile sources such as gasoline, diesel or natural gas fired vehicles due to inconveniences in ammonia storage and delivery, concerns over safety issues, and ammonia slippage (unreacted ammonia in the effluent). If hydrocarbons are used as a reductant carbon oxides will also be produced. Hydrocarbons are more likely to be used as a reductant in mobile sources. However, the invention described herein includes any reductant used in any source, whether mobile or stationary.

In another embodiment, the catalyst which is supported on the mesh-like structure is employed in the decomposition of nitrogen oxides into diatomic oxygen and diatomic nitrogen. Typical catalysts used for this purpose are transition metal and noble metal cations exchanged into zeolites, or supported on metal oxides.

In another embodiment, the catalyst which is supported on the mesh-like structure is employed in the oxidation of ammonia to form nitrogen and water (selective catalytic oxidation). This reaction can be used to remove any unreacted ammonia after selective catalytic reduction.

In another embodiment where NOx levels are low in the feed, it is advantageous to enrich the concentration of NOx in order to enhance the rate of reaction. In this embodiment, NOx is first enriched by adsorption onto a catalyst and then reacted, or adsorbed onto a catalyst-or adsorbent and then desorbed and reacted on the same or different catalyst. Often the temperatures required for adsorption and reaction are different, with low temperatures preferred for adsorption and higher temperatures preferred for reaction. Given the fast temperature changes typical of mobile sources such as automotive engines, a quick change between adsorption and reaction are required to achieve optimum system efficiency. The use of the mesh-like structure described herein is ideal for such applications given its' superior heat transfer, low thermal mass and its' ability to be heated electrically. In addition, the use of the mesh-like structure improves catalyst effectiveness and, therefore, increases volumetric activity.

For example, ammonia or urea may be reacted with NO and NO_2 found in the exhaust gases of fossil fueled power plants, or in the combustion products of internal combustion engines to produce nitrogen and water in the presence of the catalyst supported on a mesh-like structure as hereinabove described. Such reactions are as follows:

$$4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O$$

$$NO+NO_2+2NH_3 \rightarrow 2N_2+3H_2O$$
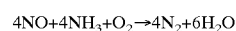
It is also possible to use a portion of the engine fuel to reduce the nitrogen oxide in those cases where it is less convenient to use ammonia or urea, such as in a mobile engine such as a typical automotive diesel engine.

$$C_xH_y+2NO+(x+y/4-1)O_2 \rightarrow N_2+y/2H_2O+xCO_2$$
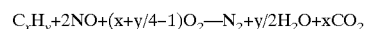
The reduction of nitrogen oxide and catalyst therefor is shown, for example in U.S. Pat. Nos. 5,750,460, 5,707,509, 5,580,534 and 5,905,056. In the present invention, such a catalyst is supported on a mesh-like material, as hereinabove described.

When used for a diesel engine, the mesh-like material that includes the catalyst for converting the nitrogen oxide(s) may be shaped into a honeycomb structure. In general, such reactions take place at a temperature of from about 100° C. to about 500° C., preferably from about 200° C. to about 400° C.

In another embodiment it is possible to catalytically decompose N_2O according to the following reaction:

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2$$
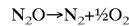
In another embodiment, an oxidation catalyst such as platinum, palladium, rhodium, cobalt, nickel, iron, copper, molybdenum, etc., and a potassium carbonate absorbent may be supported on the mesh-like structure hereinabove described. Such a combination of the catalyst, and the potassium carbonate, supported on a mesh-like structure, may be employed in oxidizing simultaneously, CO to CO_2 and NO to NO_2, according to the following reactions:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2$$
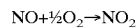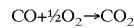
The CO and NO may be found in the exhaust gas of a natural gas-fired power plant. The NO_2 is absorbed by, and reacted with, a carbonate or bicarbonate or hydroxide, such as an alkali or alkaline earth metal carbonate, bicarbonate or hydroxide, in particular potassium carbonate, to form carbon dioxide and potassium nitrite and potassium nitrate according to the following reaction:

$$2NO_2 + K_2CO_3 \rightarrow CO_2 + KNO_2 + KNO_3$$

The potassium nitrite and potassium nitrate which remain on the catalyst, then are reacted with a reducing agent such as hydrogen gas in the absence of oxygen in order to regenerate the catalyst, in accordance with the following reaction:

$$KNO_2 + KNO_3 + 4H_2 + CO_2 \rightarrow K_2CO_3 + 4H_2O(g) + N_2$$

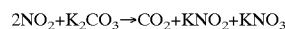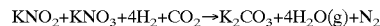Water, as steam, and elemental nitrogen are exhausted instead of NO or NO_2, and potassium carbonate once again is present as an absorbent on the mesh-like structure, thereby allowing the oxidation and absorption cycle to begin again. This process is described in U.S. Pat. Nos. 5,665,321, 5,762,885 and 5,650,127.

Various embodiments of structural packings will now be described. In FIG. 1, packing 2 is diagrammatically representative of a plurality of parallel corrugated sheets of porous mesh material (referred to herein as MEC material) in which the corrugations 4 are represented by diagonal lines which are at an angle α to the vertical direction of flow F. FIG. 1a, a representative cross section of a corrugation 6. Adjacent corrugated sheets 8 alternate 90° from each other. The MEC material is preferably metal fibers but may be ceramic or combinations thereof.

Vertical orientation of the packing relative to the flow direction F is desired to optimize the pressure drop vs. the NO removal and minimize the NH_3 slip (unreacted NH_3). This is best represented by a removal efficiency characterized by the term k/Δp where k is the first order reaction rate constant and Δp is the pressure drop. Table 1 shows the relationship between the angle of inclination Δ and the removal efficiency for different angles of inclination and also compared to a typical solid ceramic monolith honeycomb structure used for this purpose. Angle α may be in the range of about 45° to about 70°. However, a mesh honeycomb may be used in the alternative. Typical solid ceramic honeycombs, Table 1, exhibits a pressure drop at a superficial velocity of 5 m/s and 350C. of about 750 Pa/m. What is important is the degree of mixing achieved in a structure with a lower pressure drop (higher angle of inclination) which will tend to decrease ammonia slip while maintaining

NO conversion. This lower pressure drop is important in power generation systems since any additional pressure loss will decrease power generating turbine efficiency.

TABLE 1

Reaction Temperature = 300° C.			Corrugated Porous structure			
	Honeycomb		45 deg angle		60 deg angle	
GHSV	Conv	k/Δp	Conv	k/Δp	Conv	k/Δp
10000	95.9	2366	91.8	3637	89.4	7377
20000	84.3	1371	83.9	1980	84.2	4680

Reaction Temperature = 350° C.			Corrugated Porous structure			
	Honeycomb		45 deg angle		60 deg angle	
GHSV	Conv	k/Δp	Conv	k/Δp	Conv	k/Δp
10000	97.7	2794	93.9	4067	92.7	8603
20000	88.7	1615	89.2	2414	87.9	5357

Table 1 shows that although there is a slight loss in conversion in going from a structure containing a 45° angle of inclination to a structure with a 60° angle, this is overshadowed by the increase in overall efficiency. The above Table also shows that the advantage of the catalyzed porous corrugated structure over the honeycomb increases with increasing GHSV. This is due to the additional benefit of better mixing at higher throughputs for the turbulence causing corrugated structure as opposed to the laminar flow regime typical of a honeycomb.

It is believed that to further increase the conversion, a combination of corrugated porous MEC mesh material and conventional ceramic honeycomb monolith in a vertical flow orientation should be used. This is shown in FIG. 3c. However, a mesh honeycomb constructed of metal fibers or ceramic fibers or both materials, may also be used in the alternative.

In FIG. 3a, a conventional ceramic honeycomb structure 10 has a length of L_1, whereas a corrugated structure 12 using MEC mesh material of the present invention for the structure packing elements has a height of L_2 and $L_2 < L_1$ for a given conversion value. In FIG. 3c, the corrugated structure 14 is combined with a honeycomb structure 16 of generally the same construction as structures 10 and 12 except the combined lengths L_3 are now shorter to provide a given conversion provided by either the honeycomb alone of FIG. 3a or the corrugated structure of FIG. 3b. Thus improved conversion is provided while using less corrugated structure material. The use of less of the novel DeNOx structure is a compromise solution to those existing facilities which prefer a quicker revamp/turnaround at the expense of somewhat higher removal. The increase in conversion will be caused by the improved mixing of the structure creating an improved efficiency of the downstream honeycomb.

In FIG. 2, a preferred converter structure 18 comprises a housing 20 preferably square or rectangular in cross section having a chamber in which packing 22 is located. The packing 22 comprises MEC porous mesh fibrous material elements, preferably metal fibers, as described herein above.

The porous MEC material comprises a plurality of corrugated elements 24 as shown in FIG. 1 and referred to in Table 1 preferably at an inclination angle α of 45° or at any other suitable angle according to a given implementation. The elements 24 are in this embodiment identical, but may differ according to the particular implementation. In FIG. 19,

the angle of adjacent elements is defined by 2α wherein each diagonal line in the figure represent the corrugations of an element, the two crossing diagonals representing adjacent elements wherein the flow direction is as shown in FIG. 1. As seen in FIG. 4, the angle of inclination α of adjacent elements differs by 2α and alternate. No vortex generators are on the elements 24. The number of elements used depends upon the dimensions of the housing 20 and the dimensions of the corrugations and of course the sheet thickness.

In FIG. 5, in the alternative, a corrugated mesh material element 26 may be used in place of the corrugated elements 24 of FIG. 4. The element 26 has optional vortex generators 28. The element 26 of FIG. 6 is fabricated in apparatuses shown and described in the aforementioned applications PCT/US00/06137; PCT/US98/27699, the former corresponding to application U.S. Ser. No. 09/181,186 Pat. No. 6,276,045 and the latter corresponding to U.S. Ser. No. 09/002,539 Pat. No. 6,277,340 mentioned in the introductory portion herein. The latter applications provide a description of an apparatus fully incorporated by reference herein for making the elements 26 forming corrugations 32 and the vortex generators in the sheet material. The corrugations are formed by adjacent side walls 34, 36, 38, 40 and so on. The corrugations define roots 42 and crests 44. The side walls are inclined preferably at an angle β (FIG. 8) of about 90°. The roots and crests extend in a linear direction.

The elements 24, FIG. 4, are oriented with their corrugation channel axes at alternating angles to the flow direction F, FIG. 1. The corrugations form gas channels there through. These channels are in fluid communication with each other at the edges of the elements at the housing 20 peripheral surface. The flow pattern angle may be at any desired value according to a given implementation as set forth in Table 1 above at the desired minimum pressure drop. The gas entering the housing 20 in direction 21, FIG. 2, enters into the channels of the elements and then is diverted at angle a initially then at 2α thereto in the adjacent elements and so on alternating in the direction of flow. This creates a turbulence in the flow. This turbulence creates a pressure differential across the elements resulting in fluid flow through the pores of the MEC porous sheet material.

In FIGS. 6, 7 and 8, optional vortex generators 46 and 48 are triangular and bent from the plane of the element 26 sheet material. The generators 46 and 48 alternate in the direction in which they project from the plane of the sheet material as best seen in FIG. 8. The corrugations have a width w. The vortex generators provide additional turbulence and thus further promote fluid flow through the pores of the MEC material due to the pressure differential thereacross.

In FIG. 9, structured packing 102 in a further embodiment is formed of porous mesh MEC material, metal fibers or ceramic fibers or both, and comprises an array of identical packing elements 104, 106, 108 and 110 which are part of a larger array 103, FIG. 11. This packing structure shows optional vortex generators of a novel configuration. While nine elements are shown in FIG. 11, this is by way of illustration, as in practice more or fewer elements may be used according to a given implementation. Also, the elements are shown in a square array. This configuration is also by way of illustration as a preferred embodiment. In practice, the array may also be rectangular, circular or any other desired shape in plan view, comparable to the view of FIG. 11, as desired for a given implementation.

The elements are housed in an outer tower housing 112 which in this case is square in transverse section. Other

housings (not shown) may be rectangular or circular in transverse section, as shown for example in embodiments described hereinafter. Each element 104, 106, 108 and 110 is formed from an identical substrate blank 114, FIG. 13, of preferably composite porous fibers as described hereinabove. The material is preferably formed from the material as described above herein or as described in the US patents noted in the introductory portion and which are incorporated by reference herein.

The blank 114 is a fragment of and represents a portion of a larger complete blank forming each of the elements of FIG. 11. The complete blank (not shown) appears as shown for the partial blank 114 with an identical repetition of the illustrated pattern extending to the right in the Figure (and according to a given implementation, may extend further vertically from the top to bottom of the figure).

In FIG. 13, the substrate blank 114 includes a plurality of optional through cuts represented by solid lines. Fold lines are illustrated by broken lines 116, 118, 120, 160 and so on. A first row 122 of identical tabs 124 and identical through holes 126 are formed with a tab 124 and hole 126 disposed between each of alternating pairs of adjacent fold lines, such as lines 116 and 118, 120 and 121 and so on. Tabs 124 eventually form vortex generators as will be described below herein. The holes 126 are adjacent the tip region of the tabs 124 and are located on a channel forming fold line at which the inclined edge 130 emanates. The same reference numerals with or without primes and multiple primes in the figures represent identical parts.

Each tab 124 has a first edge 128 coextensive with a channel forming fold line, such as line 118. The tab 124 has a second edge 130 which emanates at a second channel fold line such as fold line 116 inclined to the fold lines 116 and 118 terminating at a distal end segment tip 132. The edges 128 and 130 terminate at one end at tab fold line 160 along plane 133. The tip 132 has an edge that is coextensive with edge 128 both of which edges are straight and lie on a channel fold line, such as line 118. The edges 128 and 130 both emanate from a common transverse plane 133 as do all of the edges of the tabs 124 of row 122. The tip 132, which is optional, preferably is square or rectangular for the purpose to be described, but may be other shapes as well according to a given implementation. Holes 126 are slightly larger than the tip 132 so as to permit a tip 132 of a tab 124 to pass therethrough in a manner to be explained. All of the tabs 124 and holes of row 122 are aligned parallel to plane 133.

Additional rows 127 and 129 of tabs 124 and holes 126 are aligned parallel to row 122 and are aligned in the same column such as column 134 between a given set of fold lines such as lines 116 and 118. The tabs 124 and holes 126 between fold lines 116 and 118 are aligned in column 134. The blank 114 as shown has alternating columns 136, 138 and so on corresponding to column 134 of tabs 124 and holes 126 which are aligned in the respective rows 127 and 129. More or fewer such rows and columns may be provided according to a given implementation.

The rows 122, 127 and 129 alternate with rows 140, 142 and 144 of tabs 124 and holes 126. The tabs 124 and holes 126 of rows 140, 142 and 144 are in the alternate columns 146, 148, 150, 139, 143, and 147. Consequently, the blank 114 has a plurality of rows and columns of the tabs 124 and holes 126 with the tabs of a given set of columns and rows alternating in vertical and horizontal position with the tabs and holes of the remaining columns and rows as shown.

In FIGS. 10 and 10a, the element 104, as are all of the elements, is formed by bending the blank substrate material

along the fold lines **116, 118, 120, 121** and so on (FIG. **13**) in alternating opposite directions. This forms the blank **114** into a channelized quasi-corrugated structure. The structure has identical preferably square in plan view channels **154, 156, 158** and so on. These channels face in alternating opposite directions **159** (FIG. **12**). Thus channels **154, 158** and so on face toward the bottom of the figure, directions **159** and channels **156, 161, 163** and so on face in the opposite direction toward the top of the figure.

In FIG. **12**, representative element **162** has channels **164, 166, 168, 170** each having a respective intermediate connecting wall **172, 174,** [1]**76** and **178** and so on lying in planes extending from left to right in the figure spaced in a normal direction. Channel **166** has lateral side walls **180** and **182** and channel **168** has lateral side walls **182** and **184** with wall **182** being in common for channels **166** and **168**. The element **162** has further identical channels as seen in FIG. **11**. All of the elements of packing **102** are constructed similarly with identical channels.

Prior to forming the channels or at the same time, the tabs **124**, FIG. **13**, are bent to extend from the plane of the blank **114** to form vortex generators at collinear fold lines **160** lying on plane **133**.

The tabs **124** in row **122** are bent out of the plane of the figure in opposite directions in alternate columns **134, 136, 138** and so on. Thus the tabs of columns **134, 138,** and **145** are bent in the same direction, e.g., out of the drawing plane toward the viewer. The tabs in columns **136** and **141** are bent in the opposite direction out of the plane of the figure away from the viewer. The same bending sequence is provided the tabs of rows **127** and **129** which are in the same columns as the tabs of row **122** so that the tabs of a given column are all bent in parallel directions.

The tabs **124'** of the next row **140** in the adjacent alternate columns **146, 148, 150** and so on are all bent parallel in the same direction at corresponding collinear fold lines **186** parallel to plane **133** toward the viewer. They are also parallel to the tabs of columns **134, 138** and so on.

The tabs **124"** of the next row **127** are bent at their respective fold lines in the same direction as the tabs **124'** in row **127**, e.g., toward the viewer out of the plane of the drawing. These tabs are parallel to the tabs of row **140**.

The tabs **124'''** of the row **142** are bent at their fold lines in a direction opposite to the bend of the tabs of rows **127** and **140**, e.g., in a direction out of the plane of the drawing away from the viewer. These tabs are parallel and bent in the same direction as the tabs in columns **136** and **141**. The tabs of row **129** are bent in the same direction as the tabs of rows **122** and **127** in the same columns, repeating such bends. The tabs of row **144** are bent the same as the tabs of rows **142** and **140** toward the viewer.

In FIGS. **9** and **10**, element **104** has a set of tabs 124_1, $124_1'$, $124_1''$, $124_1'''$, **121** and **123** in channel **154**. The tabs 124_1, $124_1''$, and **121** all extend in the same direction, for example, from channel **154** connecting wall **190** into the channel **154**. The tabs $124_1'$, and **123** extend from the same lateral side wall, e.g., side wall **192**. The tab $124_1'''$, however, extends into channel **154** from the opposite lateral side wall **194**. The tabs in plan view along the channel **154** length, from the top of the figure to the bottom, in FIGS. **9** and **10**, interrupt the vertical channels and thus form a solely tortuous generally vertical path for fluids. No open continuous vertical linear fluid path is available along the channel lengths for any of the channels.

The tabs in the next opposite facing channel **156** are in mirror image orientation to the tabs of channel **154** as best seen in FIG. **10**.

The tortuous blocking interruption of the vertical linear path by the tabs is best seen in FIG. **12**. Representative element **162** channel **166** has an uppermost tab 124_2, a next lower tab $124_2'$ and then still lower tabs $124_2''$ and 121_2, and so on. Tabs in adjacent columns in certain rows, such as row **144**, FIG. **13**, have the same orientation as the tabs in the representative channel **166** such as tabs **123**, 123_2, FIG. **10**. As shown in FIG. **12**, a portion of each of the tabs overlies a portion of the other tabs in the channel. In the plan view the channel **166** is totally blocked by the tabs, as are all of the channels, in the vertical direction normal to the plane of the figure. Thus no linear vertical fluid path is present along the length of the channel **166** (or channels **154, 156, 158** and so on in FIG. **10**). Also, each tab in a given channel has one edge thereof adjacent to and abutting either a lateral side wall or a connecting wall.

The tabs extending from an intermediate connecting wall, such as tab 124_2, FIG. **12**, attached to wall **174** of element **162**, extend toward and pass through the hole **126** of the connecting wall of the adjacent packing element, such as wall **197** of element **1102**. However, none of the tabs of element **1102** extend into or toward the channels of the element **162**. Thus, the tabs of each element are employed for substantially cooperating with only the channels of that element to provide the desired tortuous fluid paths. The tabs of each element are substantially independent of the channels of the adjacent elements, notwithstanding that the tips **132** of the connecting wall tabs cooperate as described with the connecting walls and channels of the adjacent elements.

The tabs **124** and tips **132** are not bent away from the plane of the blank **114**, FIG. **13** for those walls of the channels next adjacent to the housing, which walls abut the housing **112**. Thus the tabs at the edges of the structure array **103**, FIG. **11**, do not extend beyond the structure so as to not interfere with the housing **112** interior walls. In the same manner, the tabs at the edge surfaces of the structure **103** are not bent beyond the plane of these surfaces as shown in FIG. **11**. Holes **126** in these edge surfaces are also not necessary.

The tips **132** and holes **126** are optionally employed to provide drip flow of liquid to opposite sides of the respective channel walls to enhance fluid contact throughout the packing structure. Also, the use of vortex generators, cross communicating holes and the like are optional for the present invention.

The holes **126** also provide fluid communication among the channels in directions transverse the vertical axis of the structure array **103**. Of course, the openings in the structured elements sheet material formed by bending the tabs out of the plane of the sheet material provide major fluid communication between the channels in a transverse direction. These openings and openings **126** may be formed in all four walls of each interior channel.

The elements of structure array **103**, FIG. **11**, such as elements **104, 106, 108, 110** and so on, are preferably secured together by spot welding the corners of the channels at their upper and bottom ends. The welding is optional as the elements may be dimensioned to fit closely into the tower housing **112** (FIG. **11**) and held in place to the housing by friction or by other means (not shown) such as fasteners or the like. The elements may also be secured together first by any convenient fastening devices or bonding medium.

It should be understood that the number of tabs in a channel and their relative orientation is given by way of example. For example, only one tab, such as tab $124_1'''$ in channel **154** extends from the lateral side wall **194** into channel **154**. In practice, more than one tab would extend from each side wall into each channel. Also, the sequence of

tab orientation, e.g., which tabs extend from a given wall in a vertical sequence, is also by way of example, as other orientations may be used according to a given need.

Further, the vertical length of the elements and the packing array channels of the array **103** in practice may vary from that shown. The channel lengths are determined by the factors involved for a given implementation as determined by the type of fluids, volumes thereof, flow rates, viscosities and other related parameters required to perform the desired process as discussed hereinabove in more detail. The structure of FIGS. **9–13** is described further in the aforementioned PCT application PCT/US98/27699 incorporated in its entirety by reference herein.

In FIGS. **14**, **15** and **16**, a catalyst support structure or heat transfer modular packing **2028**, according to a given implementation, is placed axially in a tube **2020** for the length of the tube **2020**. The packings **2028** each comprise a single one piece sheet of porous mesh or screen material made of metal or other fibers. The fiber material may also be ceramic, glass, carbon or any combination thereof. The modular packings **2028** are place in preferably abutting (or closely spaced relation) in the tube **2020** ore.

Representative modular packing **2028** comprises a single sheet of the porous mesh material. The mesh material, FIG. **16**, is folded at fold lines **2030**, **2031**, **2032** and so on at one side **2034** of the packing **2028**, and at fold lines **2030'**, **2031'** and **2032'** and so on at the opposite side of the **2036** tube **2020**. Fold lines **2030**, **2030'** define a planar section **2038** therebetween of the flat planar sheet mesh material. Fold lines **2031**, **2031'** form an adjacent planar section **2040** of mesh material. Sections **2038** and **2040** form a fluid flow channel **2042** therebetween for fluid flowing nominally in direction **2044**, FIG. **14**. The actual direction of fluid flow in the tube is complex due to turbulence as will be described and also flows inclined transverse to the tube longitudinal axis defined by direction **2044**.

The region between sections **2038** and **2040**, by way of example, between fold lines **2030'** and **2031'** forms a generally rectangular intermediate tube interface **2046** which abuts the tube **2020** inner surface. The sections **2038** and **2048** which are representative of the orientation of the other sections in the packing **2028** are parallel and parallel to the other sections in the packing. As a result there is an array **2048** of parallel sections, each section terminating at a foldline forming an interface with the fold line of the adjacent section. The intermediate interfaces such as interface **2046** all abut an inner surface of the tube **202020** in preferable thermal conductive relation. The sections such as sections **2038** and **2040** and so on are all interconnected as a one piece structure separated by fold lines and an intermediate interface, such as interface **2046**.

The array of sections such as sections **2038**, **2040** and **2060** form a corresponding array of fluid channels such as channel **2042** which are all parallel of generally the same transverse width in directions **2050**, FIG. **16**. Located in each channel are turbulence generator vanes **2052**, **2054** and **2056**, for example in channel **2058**. The vanes are all inclined at about 45° with respect to the fluid flow direction **2044** through the tube **2020**, but may be inclined at other angles. The vanes redirect fluid impinging on the vanes transversely against the tube **2020** inner side wall surface to optimize heat transfer to the tube. The vanes **2052**, **2054** and **2056** are just a few of the vanes attached to section. Other like vanes are in spaced alignment with the vanes **2052**, **2054** and **2056** in the axial fluid flow direction **2044** of the tube **2020** in a vertical array. Either an interface or vane (at the edge of the packing such as vanes **2057** and **2059**, FIG.

16) is in thermal conductive contact with the inner surface of tube **2020**. The modular packing **2028** is thus a zig-zag structure folded in accordion fashion with somewhat rectangular channels formed by planar sections and intermediate interfaces. The intermediate interfaces are at angles to the plane of some of the sections so as to mate with corresponding curvature of the tube **2020** inner surface as shown in FIG. **14**.

The configuration and layout of the vanes **2052**, **2054**, **2056** and so on is best illustrated in connection with FIGS. **17** and **18**. In FIGS. **17** and **18**, the orientation of the vanes are different, but the dimensioning of the vanes is the same for a given tube internal diameter as the relative orientation of the vanes is not critical for a given tube, the orientation of all of the modules preferably being the same in a corresponding tube. However, the orientation of the vanes, which may be about 45° to the longitudinal axis of the tube may also be different for a given set of modules in a tube according to a given implementation.

In FIG. **17**, three identical rectangular blank sheets **2062**, **2062'** are formed of wire mesh from a blank **2063**, the mesh material to be described below. Representative sheet **2062'** is an elongated rectangular sheet of fiber mesh material having two parallel identical longitudinal edges **64** and parallel identical end edges **2066**. Solid lines in the blank **2063** sheet represent through cuts. The blank sheet **2062'** has a plurality of aligned sections **2068**, **2070** and **2072** and so on in a linear array. The sections have different lengths L that corresponds to the transverse dimension across the tube **2020** internal diameter for that section (see FIG. **16**). The interfaces are between each such section such as interfaces **2074**, **2076** and **2078**. The interfaces alternate on opposite sides of the tube **2020** as shown in FIG. **16**. The vanes are formed by cuts **2088**, FIG. **18**, in blank **20104** at 45° to the length dimension of the blank and sections from left to right in the figure.

As best seen in FIG. **18**, in blank **20104** the vanes such as vanes **2080**, **2082** and **2084** in representative section **2086** are identical and formed by through cuts **2088**. Vanes **2090** and **2092** are shorter than vanes **2080**, **2082** and **2084** as they are located in the corner of the section. The mirror image vanes **2094** and **2096** in the diagonal opposite corner of section **86** are the same as vanes **2090** and **2092**, but in the alternative may differ from each other according to a given implementation.

Cut **2088** has a straight portion **2088'** and an angled cut at one end of the cut and a U-shaped cut **2098** in conjunction with cut **2088'**. Representative vane **2084** has a fold line **20100** shown by the dashed line. The fold lines for the vanes in the other sections are not shown by dashed lines, but are intended to be included. The fold lines for all of the central sections in blank **20104** excluding the two opposite end sections such as section **20102** are parallel to fold line **20100**.

The sections are each separated by two fold lines such as fold lines **20106** and **20108** between sections **2086** and **20102**. Sections **20106** and **20108** form intermediate interface **20110** therebetween. A further intermediate interface **20112** is between fold lines **20114** and **20116** of respective sections **20118** and **2086** and so on.

The vanes of end section **20102** are different then the vanes intermediate the end sections. The vanes **20120**, **20122**, **20124** and so on of the end section **20102** are thinner in transverse width, and have curved external edges **20128**. These vanes directly abut the inner surface of the tube and therefore have curvatures that match the curvature of the curved inner surface of the tube **2020**. These end section vanes correspond in location to vanes **2054**, **2057**, for

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example, in FIG. 16, modular packing 2028. It should be understood that the drawings are not to scale and are generally schematic in nature to explain the principles rather than provide exact dimensional relation of the different elements of the packing and tube 2020.

Because the vanes of the different modular packings 2028, FIGS. 14–16, are inclined generally at 45° to the longitudinal axis of the tube 2020, these vanes all direct fluid against the inner surface of the tube wall to maximize heat transfer from the interior of the sections to the tube. The vanes also create local pressure differentials, i.e., turbulence, which may maximize fluid flow through the mesh of the substrate material forming the modular packing 2028 as will be described in more detail herein. The mesh material because of the small pore size normally does not exhibit fluid flow therethrough when the pressure differential thereacross on opposite surfaces is about the same or a small value.

The size and spacing of the openings in the mesh material of the sections, preferably in combination with the vane turbulence generators, are optionally selected to obtain a desired bulk mixing and pressure drop through the mesh of the structured packing, although such openings and generators are not necessary for the present embodiment.

The invention now will be described with respect to the following examples; however, the scope of the present invention is not intended to be limited thereby.

EXAMPLE 1

A NO_x conversion catalyst comprised of a mixture of transition metal oxides is ground in an Eiger ball mill for five minutes at 4000 rpm to make a slurry of 19.6 weight percent solids to produce a mean particle size of 2.4 micron. To this slurry mixture 2 weight % of Nyacol alumina sol was added on the basis of the solids weight in the slurry. A Hastelloy X microfiber sheet of 0.4 millimeter thickness and 90% porosity was formed into a honeycomb structure that was then coated with this slurry mixture by dip coating of the structure. The excess slurry in the channels was removed by air knife treatment at 5 bar pressure. The structure weighed 6.14 grams prior to coating and 7.25 grams after coating and drying at 120° C. for 1 hour, thus giving a weight percent pickup of 15.4 weight percent. This coated honeycomb was then coated a second time with the same air knife removal of slurry from the honeycomb channels. The second coating resulted in a honeycomb with a weight of 8.40 grams which yields a sample of 26.9 weight percent. Two more honeycomb structures of 6.32 and 8.43 grams weight were coated as described in this example and the final weight percent of these two sample were 27.9 and 28.6%. These samples were used for catalytic evaluation of NOx removal in a simulated exhaust gas and were shown to be effective catalysts for removal of NOx.

EXAMPLE 2

To sixty grams of the slurry mixture in Example 1, sixty grams of water was added to dilute the solid content in the slurry to 9.8 weight percent. A honeycomb of 5.87 grams was coated with the 19.6 weight percent slurry of Example 1, and dried as described in Example 1. This honeycomb structure was then coated a second time with the 9.8 weight percent slurry, and air knifed as described in Example 1. This second coating resulted in a final loading level of 21.2 weight percent. This sample was used for catalytic evaluation of NOx removal in a simulated exhaust gas, and was shown to be an effective catalyst for removal of NOx.

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EXAMPLE 3

A second batch of the catalyst was ball milled as described in Example 1 for 5 minutes. To this slurry was added 1 weight percent Povidone (PVP) (a water soluble polymer product by BASF) based on the total slurry concentration. To this slurry was added 5 weight percent Nyacol alumina sol based on the solids content in the slurry. The solids content was found to be 23.1 weight percent. For two honeycomb structures made from the microfiber material used in Example 1, dip coating of this 23.1% slurry produced a coated product containing 20.5 and 19.8 weight percent solids after drying at 120° C. for 0.5 hour, and calcination at 500° C. for 1 hour. To a third honeycomb structure this 23.1 weight percent slurry was diluted to 17.8 weight percent, and the coated product had a loading level of 16.3 weight percent. These samples were used for catalytic evaluation of NOx removal in a simulated exhaust gas, and were shown to be effective catalysts for removal of NOx.

EXAMPLE 4

A packing of the following specifications was made:

Reactor size	
Reactor width	0.05 m
Reactor depth	0.05 m
Bundle height	0.09 m
Bundle volume	2.25E– m³ 04
No. of bundles	2
Sheets/bundle	10
Reactor total height	0.18 m
Reactor total volume	4.50E– 04m³
Packing specific surface area	500 m²/m³
Packing material	
Fiber diameter	12 μm
Sheet thickness	0.8 mm
Porosity	90%
Material	316 Stainless Steel

and the catalyst coated in the following way:

The DeNOx catalyst was ground with a ball-mill to an average particle size smaller than 5 μm. The catalyst was mixed with water in a weight ratio of 15:85, and homogenized in a ball mill with zirconia balls. The pH of the slurry was adjusted to 8.5 by addition of ammonia. The slurry was transferred to a coating bath which contained two electrodes connected to the positive poles of a power supply. Each sheet of the bundle was coated separately. The sheet was placed vertically parallel to and at equal distance from each of the electrodes and connected to the negative pole of the power supply. The coating was deposited at 9V for 30 seconds. The sheet was taken from the bath, and dried in air at 100° C. for 30 minutes, after which it was calcined in air at 500° C. for 30 minutes at a heating rate of 10° C./min.

EXAMPLE 5

The performance of a novel Selective Catalytic Reduction (SCR) DeNOx catalyst structure of the configuration described in Example 4 was used in a standard DeNOx activity test using the following conditions: an inlet NOx concentration of 500 ppm, NH3 feed of 1.1 x stoichiometric, temperature of 350° C., space velocity of 10000 l/h and a pressure drop of 1.5 mbar/m (0.06 psi/ft). Under these

conditions a NOx reduction efficiency of 92% was measured for this catalyst structure containing 0.16 g vanadium. This can be compared to the same catalyst configured as a honeycomb (35 cpsi, 2.3 g vanadium) giving a NOx removal efficiency of 96% under the same reaction conditions.

The DeNOx reaction is generally believed to first order with respect to NOx Therefore the catalyst structure of this example reaches a comparable NOx removal at a first order removal rate/unit catalyst that is 11 times faster than that of a conventional structure.

EXAMPLE 6

In this example the performance of the same catalyst structure as in Example 2 has been used to study NOx removal efficiency for low NOx applications. A gas stream containing 27 ppm NOx has been treated over the catalyst structure after ammonia injection at two different points upstream of the reactor. In the first case the resulting inlet gas stream is well mixed, in the second case NOx and NH_3 are poorly mixed before entering the catalyst structure. The results of these experiments (run under the same conditions as in Example 5 except for NOx and NH_3 concentrations) are summarized in the table below:

	Perfect Mixing Honeycomb	MEC	Poor Mixing Honeycomb	MEC
NOx, IN (ppm)	26.5	27	27	27
Removal Efficiency (%)	84	86	18	87
NOx, OUT (ppm)	4	4	22	4
NH_3, OUT (ppm)	3	3	22	3

The mesh-like SCR DeNOx structure can guarantee very low amounts of NOx and NH_3 in the outlet of streams that are not perfectly premixed. This is not true of the conventional system, where performance falls off drastically if perfect premixing is not achieved.

EXAMPLE 7

A mesh type SCR-DeNOx corrugated structure was compared to a standard straight channel solid ceramic honeycomb at conditions simulating the exit of a Gas Turbine. Both structures utilized the same catalyst (3% V_2O_5 on WO_3/TiO_2. Pressure drop in all cases is 740–840 Pa/m. Temperature—350C.
NO in—20–30 ppm
NH_3/NO in—0.92–1.0
Test Reactor Cross Section—86×90 mm
Test Reactor Length—740–750 mm
Superficial Velocity—6.4 m/s
Mesh Type Structure
500 m2/m3 sheet surface
Catalyst loading=0.19 (wt catalyst/wt catalyst+wt mesh)
Corrugation angle=60 deg relative to horizontal
Honeycomb Catalyst
882 m2/m3
45.9 cpsi
The specific rate constant in the results below takes into account differences in NH_3/NO inlet.
k/SV=−ln (1−x/r)
where k=specific rate constant (1/h)

SV=space velocity (vol feed/vol structure)
x=NO conversion
r=NH_3/NO inlet
Results

Catalyst	Reactor Length (mm)	NO in (ppm)	NH3/NO	NO Conversion	NH3slip (ppm)	k (1/h)
Honeycomb	740	26	0.92	80.4%	0.7	27800
Mesh Like	750	21	0.95	86.90	0.7	33153

This example clearly shows that a mesh type corrugated structure is able to remove more NO than a solid ceramic honeycomb structure of the same volume.

EXAMPLE 8

In the following, example the top 250 mm of the ceramic solid honeycomb structure was removed and replaced, in one case by a catalyzed mesh like corrugated structure and in another by an uncatalyzed metal foil of the same corrugated configuration. This was done in order to assess the impact of improved mixing prior to the honeycomb on ammonia slip (unreacted ammonia).

		Results			
Catalyst (1/h)	Reactor Length (mm)	NO in NH3/NO (ppm)	NO	NH3slip Conversion	k (ppm)
60 deg mesh + 29270 Honeycomb	750	25	0.99	87.7%	0.3
60 deg Foil + 29201 Honeycomb	750	28	0.95	83.40	1.25

The results of this example show that a catalyzed mixer corrugated element in combination with a straight channel honeycomb is much more effective in converting ammonia than an uncatalyzed corrugated mixer followed by a straight chain solid ceramic honeycomb. In addition, comparison of examples 7 and 8 shows that the use of mixer (catalyzed or uncatalyzed) corrugated structure plus honeycomb is more efficient in removing NOx than the same length of honeycomb alone.

EXAMPLE 9

A 25% (by wt. of solids) slurry of a V_2O_5—WO_3/TiO_2 catalytic material was prepared by ball milling to <1 micron size. The solids content of the slurried material was reduced to 10% by addition of deionized water. To this slurry, 2% (by wt. based on the solids content of the slurry) of nitric acid stabilized zirconia sol was added. Additionally, 1% (by wt. based on the weight of the slurry) of ammonium sulfate was also added to this slurry.

Sheets, 2.5 cm by 3.5 cm 0.8 mm thick, 95% void volume, made of high purity silica fibers were coated using this slurry. The sheets were then dried at 120° C. for 1 h. A second coating of catalyst from the slurry was performed and the sheets dried again at 120° C. for 1 h. The dried sheets were calcined at 350° C. for 4 h. The uptake of catalytic material on the silica fiber sheets was found to be 70%

(based on the final wt. of the coated sheet). The catalyst thus prepared was tested for its NO reduction capability.

The conditions of the testing were:

NO Concentration: 410 ppm

NH_3 Concentration: 390 ppm

Oxygen Concentration: 5%

CO_2 Concentration: 13%

H_2O Concentration: 8%

NO conversion of 86% was observed at a temperature of 300° C. and a space velocity of 25000 h^{-1}.

The disclosures of all publications, including patents and published patent applications, are herein incorporated by reference to the same extent as if each publication were specifically and individually incorporated herein by reference.

It is to be understood, however, that the scope of the present invention is not to be limited to the specific embodiments described above. The invention may be practiced other than as particularly described and still be within the scope of the accompanying claims.

What is claimed is:

1. A process for removing at least one nitrogen oxide from a fluid, comprising:

forming a mesh structure of a porous material having internal pores and opposing sides, the average pore size of the material being sufficiently small that normally fluid flow is not exhibited through the porous material in the presence of negligible pressure differential thereacross on opposite surfaces, said mesh structure having a porosity of greater than about 85%, the opposing sides forming channels, each channel having a fluid receiving inlet and a fluid outlet, the received fluid for flowing through the channels along the surfaces of the material to and through said outlets from the respective inlets, the pores being in fluid communication with each other and with the channels externally the material at each said side, said material including turbulence generator means one piece therewith for creating a pressure differential across the opposing sides in said flowing fluids, said pressure differential for causing the flowing fluids to flow through the pores transversely

through the material from one side to the other side of the material to promote contact between the fluids flowing on the opposite sides of the material and to promote contact with the material in the pores over essentially the entire surface of the material; and

supporting a nitrogen oxide conversion catalyst on the material on the opposing surfaces and in said pores for reacting with said fluids as the received fluids flow through the channels and through the pores from one side to the opposite side of the material over essentially the entire surface of the material.

2. The process of claim **1** wherein said at least one nitrogen oxide is selected from the group consisting of NO and NO_2 and N_2O.

3. The process of claim **1** wherein the supporting step comprises coating the catalyst onto the mesh structure.

4. The process of claim **3** wherein the coating thickness is less than 30 microns.

5. The process of claim **1** wherein the step of forming the mesh structure includes forming the mesh structure of at least one of a fibrous metal, ceramic-metal or ceramic.

6. The process of claim **1** wherein the step of forming the mesh structure includes forming corrugations in the mesh structure, the corrugations forming said channels, the step of forming the mesh structure including orienting said channels to each other to form said turbulence generator means.

7. The process of claim **1** including the steps of forming the mesh structure into a corrugated structure, forming the corrugated structure into turbulence generator means and then flowing the fluid through a series arrangement of the corrugated structure and a monolith honeycomb structure.

8. The process of claim **1** comprising: oxidizing the at least one NO to NO_2 and contacting the NO_2 with a metal carbonate, bicarbonate or hydroxide supported on the mesh structure, said mesh structure comprising one of a metal, ceramic and ceramic/metal and having a porosity of at least 87%.

9. The process of claim **1** wherein said mesh structure has a porosity of greater than 90%.

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