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(54) **EXTRUDED SCR FILTER**

EXTRUDIERTES SCR-FILTER

FILTRE DE RÉDUCTION CATALYTIQUE SÉLECTIVE (RCS) EXTRUDÉ

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Description

[0001] The present invention relates to a wall-flow filter comprising an extruded solid body for use in treating oxides of nitrogen in exhaust gas emissions from internal combustion engines from stationary source and mobile applications.

[0002] EP 1739066 discloses a honeycomb structure comprising multiple honeycomb units having multiple through holes; and a seal layer that joins honeycomb units with each other via respective closed outer faces of the honeycomb units where the through holes are not open. The honeycomb unit includes at least inorganic particles, inorganic fibres and/or whiskers. The inorganic particles exemplified are alumina, titania, silica and zirconia; the inorganic fibres exemplified are silica alumina fibres; and the inorganic binders exemplified are silica sol, alumina sol, sepiolite and attapulgite. A catalyst component can be carried on the honeycomb structure. The catalyst component may include at least one type selected among noble metals including platinum, palladium and rhodium, alkali metals such as potassium and sodium, alkaline earth metal e.g. barium and oxides. The honeycomb structure can be used as a catalytic converter e.g. a three-way catalyst or a NO_x storage catalyst for conversion of the exhaust gas of vehicles.

[0003] WO 2009/093071 discloses a wall-flow filter monolith substrate having a porosity of at least 40% formed from a selective catalytic reduction catalyst of extruded type.

[0004] US 7,507,684 discloses an extruded monolithic catalytic converter for converting oxides of nitrogen in the presence of a reducing agent and a method of manufacturing such an extruded monolithic catalytic converter.

[0005] WO 2009/001131 discloses a method of converting nitrogen oxides in a gas stream to nitrogen comprising contacting the nitrogen oxides with a nitrogenous reducing agent in the presence of a non-zeolite base metal catalyst consisting of: (a) at least one transition metal dispersed on a mixed oxide or composite oxide or a mixture thereof as support material consisting of cerium and zirconium; or (b) cerium oxide and zirconium oxide as single oxides or a composite oxide thereof or a mixture of the single oxides and the composite oxide dispersed on an inert oxide support material, on which inert support material is also dispersed at least one transition metal.

[0006] WO 2009/0143221 discloses zeolite-based honeycomb bodies and methods of manufacturing them. The zeolite-based honeycomb bodies are said to be especially suited for engine exhaust treatment applications and include a primary phase comprising a zeolite having a SiO_2 to Al_2O_3 molar ratio in the range from 5 to 300. The zeolite-based composites are said to be porous with an open porosity of at least 25% and a median pore diameter of at least 1 micron and can be manufactured by an extrusion method.

[0007] We have now developed a family of catalysts comprising an extruded solid body and at least one metal with particular application in the field of exhaust gas aftertreatment of internal combustion engine exhaust gas. Such exhaust gases may result from stationary source emissions, but they have been developed for use in particular for treating mobile sources of emissions, such as passenger cars, trucks and buses.

[0008] According to one aspect, the invention provides a wall-flow filter comprising a catalyst for converting oxides of nitrogen in the presence of a reducing agent, which wall-flow filter comprising an extruded solid body comprising: 10-90% by weight of at least one binder/matrix component; 5-95% by weight of a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof; and 0-80% by weight optionally stabilised ceria, which catalyst comprising at least one metal, wherein: (i) the at least one metal is present throughout the extruded solid body and is also present in a higher concentration at a surface of the extruded solid body; (ii) the at least one metal is present throughout the extruded solid body and is also carried in one or more coating layer(s) on a surface of the extruded solid body; or (iii) the at least one metal is present throughout the extruded solid body, is present in a higher concentration at a surface of the extruded solid body and is also carried in one or more coating layer(s) on the surface of the extruded solid body.

[0009] An advantage of the present invention is that by removing catalytic components that are often used in catalytic coatings, the number of coatings can be reduced, e.g. from two layers to one layer; or a single layer can be removed altogether and catalytic metal can be supported on a surface of the extruded solid body as such. This has benefits in reducing backpressure in an exhaust system, increasing the efficiency of the engine.

[0010] Furthermore, by providing the possibility of uncoated catalysts, the extruded solid body can be manufactured at higher cell density, increasing strength and decreasing the thickness of cell walls which can improve light off performance and increase activity through mass transfer.

[0011] Also it is possible to increase the volume of active components in an extruded solid body relative to a coating on an inert substrate monolith. For example, a typical catalytic coating of a non-zeolitic molecular sieve-based catalyst for reducing oxides of nitrogen using a nitrogenous reductant on an inert substrate monolith is about 2.2 g in^{-3} (134.3 g/l), whereas the same catalyst can be extruded at 7.5g in^{-3} (457.7 g/l). We have also found that catalysts disclosed in our WO 2009/001131 disclosed above can be coated at about 2.7 g in^{-3} (164.8 g/l), whereas the equivalent material can be extruded as a solid body at 12 g in^{-3} (732.3 g/l). This increased catalyst density has advantages for long term durability and catalyst performance, which is important for on-board diagnostics.

[0012] "On board diagnostics" (OBD) in the context of a motor vehicle is a generic term to describe the self-diagnostic and reporting capability of the vehicle's systems provided by a network of sensors linked to a suitable electronic management system. Early examples of OBD systems would simply illuminate a malfunction indicator light if a problem were

detected, but it provided no information on the nature of the problem. More modem OBD systems use a standardised digital connection port and are capable of providing information on standardised diagnostic trouble codes and a selection of real-time data, which enable rapid problem identification and resolution of a vehicle's systems.

[0013] Current OBD requirements require that a driver must be notified in case of a malfunction or deterioration of the emission system that would cause emissions to exceed mandatory thresholds. So, for example, the OBD limits for Euro 4: 98/69/EC for passenger diesel vehicles (category M vehicles as defined by 70/156/EEC) are: carbon monoxide (CO) - 3.2g/km; hydrocarbons (HC) - 0.4 g/km; nitrogen oxides (NO_x) - 1.2 g/km; and particulate matter (PM) 0.18 g/km. For passenger petrol (gasoline) vehicles, the Euro 4 limits are: CO - 3.2 g/km; HC - 0.4 g/km; NO_x - 0.6 g/km; and PM - no limit.

[0014] Future vehicular emissions legislation, especially in US and Europe, requires higher sensitivity in diagnostic function so as continuously to monitor the ability of an exhaust system aftertreatment catalyst to meet the emission legislation. For example, the current draft OBD limits for Euro 5: 715/2007/EC for compression ignition (diesel) passenger vehicles are: CO - 1.9 g/km; non-methane hydrocarbons (NMHC) - 0.25 g/km; NO_x - 0.54 g/km; PM - 0.05 g/km; and for positive ignition (gasoline) passenger vehicles: CO-1.9 g/km; NMHC - 0.25 g/km; NO_x - 0.54 g/km; and PM - no limit.

[0015] In US it is understood that the OBD II legislation (Title 13, California Code Regulations, Section 1968.2, Malfunction and Diagnostic System Requirements for 2004 and Subsequent Model-Year Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles and Engines) for catalyst monitoring of gasoline/spark ignited engines requires a malfunction signal where the average Federal Test Procedure (FTP) test for NMHC conversion efficiency of a monitored portion of a catalyst system falls below 50%.

[0016] Extruded solid bodies according to the present invention generally comprise a unitary structure in the form of a honeycomb having uniform-sized and parallel channels extending from a first end to a second end thereof. Generally, the channels are open at both the first and second ends - a so-called "flow through" configuration. Channel walls defining the channels are porous. Typically an external "skin" surrounds a plurality of the channels of the extruded solid body. The extruded solid body can be formed from any desired cross section, such as circular, square or oval. Individual channels in the plurality of channels can be square, triangular, hexagonal, circular etc. Channels at a first, upstream end can be blocked e.g. with a suitable ceramic cement, and channels not blocked at the first, upstream end can also be blocked at a second, downstream end to form a so-called wall-flow filter. Typically, the arrangement of the blocked channels at the first, upstream end resembles a chequer board with a similar arrangement of blocked and open downstream channel ends.

[0017] It is clear that the honeycomb structure disclosed in EP 1739066 has a Thermal Shock Parameter (TSP) too low to be used in a single unitary extrudate, because the honeycomb structure comprises an assembly of individual honeycomb units cemented together. This arrangement, also seen in commercially available silicon carbide honeycombs, is designed to avoid catastrophic catalyst substrate failure due to *inter alia* thermal shock as a result of a relatively high Coefficient of Thermal Expansion (CTE) of the extruded material. However, the manufacture of a honeycomb structure from individual honeycomb units is complicated, laborious, time consuming and expensive and increases the number of possible physical failure modes, e.g. at the cement bonds, compared with a single piece extrusion. A more complete explanation of TSP and CTE can be found in "Catalytic Air Pollution Control - Commercial Technology", Second Edition, R.M. Heck et al., John Wiley & Sons, Inc., New York, 2002 Chapters 7 (in relation to flowthrough monoliths) and 9 (for wall-flow filters).

[0018] Accordingly, we prefer that the extruded solid body of the catalyst according to the invention has an axial Thermal Shock Parameter (TSP) and a radial TSP sufficient to avoid radial cracks and ring cracks in the extruded solid body when used for treating exhaust gases from a stationary or mobile source of emissions. In this way the extruded solid body can be formed from a single unitary extrudate. For extruded solid bodies having a particularly large cross-section, it may still be necessary to extrude segments of the extruded solid body for cementing together. However, this is because of difficulties in processing extrudates of such a large cross section, or because of limitations in the size of the extrudate die tooling. Taken individually, however, each segment of the whole catalyst would meet the functional limitation that the axial TSP and the radial TSP are sufficient to avoid radial cracks and ring cracks in the individual extruded solid body segments when used for treating exhaust gases from a stationary or mobile source of emissions. In one embodiment the radial TSP is >0.4 at 750°C, such as >0.5, >0.6, >0.7, >0.8 >0.9 or >1.0. At 800°C, the radial TSP is desirably also >0.4 and at 1000°C is preferably >0.8.

[0019] The CTE of wall-flow filters is preferably 20 x 10^{-7}/°C in order to be formed from a one-piece extrudate.

[0020] In embodiments, the at least one binder/matrix component can be selected from the group consisting of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, a spinel, an optionally doped alumina, a silica source, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof.

[0021] Spinels can be $MgAl_2O_4$ or the Mg can be partially replaced by a metal from the group consisting of Co, Zr, Zn or Mn. In embodiments the content of MgO in the $MgAl_2O_4$ relative to Al_2O_3 can be from 0.8 to 2.5, with values of <1.0 preferred.

[0022] The alumina binder/matrix component is preferably gamma alumina, but can be any other transition alumina, i.e. alpha alumina, beta alumina, chi alumina, eta alumina, rho alumina, kappa alumina, theta alumina, delta alumina,

lanthanum beta alumina and mixtures of any two or more such transition aluminas.

[0023] It is preferred that the alumina is doped with at least one non-aluminium element to increase the thermal stability of the alumina. Suitable alumina dopants include silicon, zirconium, barium, lanthanides and mixtures of any two or more thereof. Suitable lanthanide dopants include La, Ce, Nd, Pr, Gd and mixtures of any two or more thereof.

[0024] Sources of silica can include a silica, a silica sol, quartz, fused or amorphous silica, sodium silicate, an amorphous aluminosilicate, an alkoxysilane, a silicone resin binder such as methylphenyl silicone resin, a clay, talc or a mixture of any two or more thereof.

[0025] Of this list, the silica can be SiO_2 as such, feldspar, mullite, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-berylia, silica-titania, ternary silica-alumina-zirconia, ternary silica-alumina-magnesia, ternary-silica-magnesia-zirconia, ternary silica-alumina-thoria and mixtures of any two or more thereof. Alternatively, the silica can be derived from calcining tetramethyl ortho silicate (TMOS) added to the extrusion composition.

[0026] Suitable clays include fullers earth, sepiolite, hectorite, a smectite, a kaolin and mixtures of any two or more thereof, wherein the kaolin can be chosen from subbentonite, anauxite, halloysite, kaolinite, dickite, nacrite and mixtures of any two of more thereof; the smectite can be selected from the group consisting of montmorillonite, nontronite, vermiculite, saponite and mixtures of any two or more thereof; and the fullers earth can be montmorillonite or palygorskite (attapulgite).

[0027] Inorganic fibres are selected from the group consisting of carbon fibres, glass fibres, metal fibres, boron fibres, alumina fibres, silica fibres, silica-alumina fibres, silicon carbide fibres, potassium titanate fibres, aluminum borate fibres and ceramic fibres.

[0028] The or each zeolitic molecular sieve or the or each non-zeolitic molecular sieve can be selected from the framework type code ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOF, BOG, BPH, BRE, BSV, CAN, CAS, CDO, CFI, CGF, CGS, CHA, -CHI, -CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EON, EPI, ERI, ESV, ETR, EUO, EZT, FAR, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, IHW, IMF, ISV, ITE, ITH, ITR, ITW, IWR, IWS, IWV, IWW, JBW, JRY, KFI, LAU, LEV, LIO, -LIT, LOS, LOV, LTA, LTF, LTL, LTN, MAR, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MOZ, MRE, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NES, NON, NPO, NSI, OBW, OFF, OSI, OSO, OWE, -PAR, PAU, PHI, PON, RHO, -RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBN, SBS, SBT, SFE, SFF, SFG, SFH, SFN, SFO, SFS, SGT, SIV, SOD, SOF, SOS, SSF, SSY, STF, STI, STO, STT, STW, -SVR, SZR, TER, THO, TOL, TON, TSC, TUN, UEI, UFI, UOS, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, -WEN, YUG, ZON as defined by the Structure Commission of the International Zeolite Association and mixtures of any two or more thereof.

[0029] In preferred embodiments, the zeolitic molecular sieve or the non-zeolitic molecular sieve has a maximum 8-ring pore opening structure as defined by the Structure Commission of the International Zeolite Association.

[0030] In one embodiment, zeolites for use in the present are not A-, X- or Y-zeolites, mordenite, beta, ZSM-5 or USY. That is, these zeolites may be excluded from the scope of the claims.

[0031] Preferred zeolitic and non-zeolitic molecular sieves are selected from the group consisting of AEI, AFT, AFX, BEA, CHA, DDR, ERI, FAU, FER, ITE, ITW, KFI, LEV, LTA, MER, MFI, MOR, MTS, NSI, PAU, PHI, RHO, RTH, STI, SZR, UFI and mixtures of any two or more thereof.

[0032] Particularly preferred zeolitic or non-zeolitic molecular sieves are selected from the group consisting of AEI, BEA, CHA, ERI, FER, MFI, NSI, STI and mixtures of any two or more thereof. Particularly preferred zeolitic molecular sieves are ZSM-5, beta, ferrierite, SSZ-13 and mixtures of any two or more thereof.

[0033] Although natural zeolitic molecular sieves can be used in the present invention, we prefer synthetic aluminosilicate zeolitic molecular sieve having a silica-to-alumina ratio of 10 or greater, for example 15 to 150, 20 to 60 or 25 to 40 for improved thermal stability.

[0034] In an alternative embodiment, the zeolitic molecular sieve or the non-zeolitic molecular sieve is an isomorph containing one or more substituent framework metal. In this embodiment, the or each substituent framework metal can be selected from the group consisting of As, B, Be, Ce, Co, Cu, Fe, Ga, Ge, Li, Mg, Mn, Zn and Zr, with Ce, Cu and Fe. Again, preferred isomorphic zeolitic or non-zeolitic molecular sieves can be selected from the group consisting of AEI, BEA, CHA, ERI, FER, MFI, NSI, STI and mixtures of any two or more thereof, with BEA including Fe in its framework particularly preferred. It will be understood that the process of manufacturing such isomorphs containing one or more substituent framework metal, the or each metal may be present in the final product either solely in the framework or in the framework and ion-exchanged.

[0035] Silica-to-alumina ratios in isomorphs containing one or more substituent framework metal can be >25, such as 30 to 100 or 40 to 70. By contrast, the isomorph can have a silica-to-framework metal ratio of >20, such as from 30 to 200 or 50 to 100.

[0036] In a preferred embodiment, the non-zeolitic molecular sieve is an aluminophosphate, including AlPOs, metal substituted AlPOs (MeAlPOs), silicoaluminophosphates (SAPOs) or a metal substituted silicoaluminophosphates (MeAPSOs). Preferred non-zeolitic molecular sieves include SAPO-18, SAPO-34, SAPO-44 and SAPO-47.

[0037] Silica-to-alumina ratios of the aluminophophates are generally much lower than aluminosilicate zeolites sharing the same framework type code. Typically, the silica-to-alumina ratio of aluminophosphates is <1.0, but can be <0.5 or even <0.3.

[0038] The ceria component can be optionally stabilised with at least one non-cerium element to increase the thermal stability of the ceria. Suitable ceria stabilisers include zirconium, lanthanides and mixtures of any two or more thereof. Lanthanide stabilisers include La, Nd, Pr, Gd and mixtures of any two or more thereof. The CeO_2:ZrO_2 ratio by weight can be e.g. between 80:20 or 20:80. Commercially available materials include 30% by weight CeO_2, 63% ZrO_2, 5% Nd_2O_3, 2%La_2O_3; and 40% CeO_2, 50% ZrO_2, 4% La_2O_3, 4% Nd_2O_3 and 2% Y_2O_3.

[0039] Broadly, the at least one metal can be: (a) present throughout the extruded solid body, i.e. the at least one metal is present in the extrudate composition; (b) present in a higher concentration at a surface of the extruded solid body; and/or (c) carried in one or more coating layer(s) on a surface of the extruded solid body in features (i), (ii) and (iii), is different from the at least one metal present in each of the other location(s) at (a), (b) and (c). So the at least one metal can be present at location (a) plus (b), (a) plus (c) or (a) plus (b) plus (c). Where the at least one metal is present in (a) and (b), (a) and (c) or (a), (b) and (c), the at least one metal in each location can be the same or different.

[0040] Where the at least one metal is present in location (a), i.e. throughout the extruded solid body, the at least one metal can be associated, where present, with a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof. An example of "associated with" includes being ion exchanged with the zeolitic molecular sieve component, the non-zeolitic molecular sieve component or either or both of the zeolitic molecular sieve component and the non-zeolitic molecular sieve components in the mixture. It is also possible in mixtures of two or more molecular sieves to have the at least one metal associated with one molecular sieve and not the other. For example, a first molecular sieve can be ion-exchanged with copper, dried and calcined and then mixed with a different molecular sieve with no associated additional metal.

[0041] Alternatively, one of two molecular sieves in a mixture can be associated, e.g. ion exchanged, with a first at least one metal and then a second at least one metal can be added to the extrudate composition, i.e. the second at least one metal is not specifically associated with the second molecular sieve.

[0042] Suitable at least one metal(s) to associate with the or each molecular sieve component can be selected individually from the group consisting of a transition metal, a lanthanide or a mixture of any two or more thereof. Suitable transition metals include Group IB metals, Group IVB metals, Group VB metals, Group VIIB metals and Group VIII metals. Preferably the at least one transition metal is selected from the group consisting of Fe, Cu, Ce, Hf, La, Mn, Pt, Au, Ag, In, Rh, V, Ir, Ru, and Os and mixtures of any two or more thereof. The lanthanide metal can be La, Pr, Ce and mixtures of two or more thereof.

[0043] The total metal content in the at least one metal associated with the or each molecular sieve component is from 0.1 to 20% by weight, such as from 1 to 9% by weight.

[0044] The at least one metal present: throughout the extruded solid body but not associated with the or each molecular sieve; in the majority of the at least one metal located at the surface of the extruded solid body; in one or more coating layer(s) on the surface of the extruded solid body; or in the higher concentration at the surface of the extruded solid body can be selected from the group consisting of an alkali metal, an alkaline earth metal, a transition metal, a lanthanide or a mixture of any two or more thereof.

[0045] Suitable coatings for supporting catalytic metals for use in the present invention include one or more of alumina (Al_2O_3), particularly γ-alumina, silica (SiO_2), titania (TiO_2), ceria (CeO_2), zirconia (ZrO_2), vanadia (V_2O_5), lanthana (La_2O_3) and zeolites. The ceria and alumina can be optionally stabilised using the same stabilisers as used for the extruded solid body. Suitable catalytic metals include one or more of the precious metals (Au, Ag and the platinum group metals, including Pt, Pd and Rh)).

[0046] Techniques for locating at least one metal in higher concentration at the surface of the extruded solid body include impregnation, preferably thickened impregnation, i.e. an impregnation medium thickened with a rheology modifier. Drying methods can also be used to concentrate metals at a surface of the extruded solid body. For example, a so-called "egg shell" technique, where metals are concentrated at the surface can be obtained by drying the impregnated extruded solid body relatively slowly so that the metals are deposited at the surface by wicking. Particular choices of salts and pH conditions can also be used to direct metal deposition, e.g. by determining the isoelectric point of the extruded solid body and then using the correct combination of pH and metal salts to benefit from an electrostatic attraction between cations or anions in the metal salts and the extruded solid body.

[0047] The total metal content throughout the extruded solid body but not associated with the or each molecular sieve component; located at the surface of the extruded solid body; and/or in the higher concentration at the surface of the extruded solid body can be from 0.1 to 20% by weight, such as from 1 to 9% by weight.

[0048] The total metal content of the extruded solid body, i.e. including any metal associated with the or each molecular sieve, can be from 0.1 to 25% by weight, such as from 1 to 15% by weight.

[0049] The total metal content of the catalyst as a whole, including one or more coating layer(s) on a surface of the extruded solid body comprises at least one metal, can be from 0.1 to 30% by weight, such as from 1 to 25% by weight.

[0050] In specific examples, the catalyst according to the invention comprises an extruded solid body comprising:

10-95% by weight of a cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, an optionally doped alumina, a silica source, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof;
0-80% by weight of spinel;
5-90% by weight of a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof, each optionally containing one or more metal;
0-80% by weight optionally stabilised ceria; and
0-25% by weight inorganic fibres.

[0051] The content of the at least one binder/matrix component can be >15% by weight, > 20% by weight, >30% by weight, >35% by weight, >40% by weight, >45% by weight, >50% by weight, >55% by weight, >60% by weight, >65% by weight or >70% by weight, >75% by weight, >80% by weight, >85% by weight or >90% by weight.

[0052] The content of the spinel can be >10% by weight, >15% by weight, >20% by weight, >30% by weight, >35% by weight, >40% by weight, >45% by weight, >50% by weight, >55% by weight, >60% by weight, >65% by weight or >70% by weight.

[0053] The content of the total content of the molecular sieve(s) can be >5% by weight, >10% by weight, >15% by weight, >20% by weight, >30% by weight, >35% by weight, >40% by weight, >45% by weight, >50% by weight, >55% by weight, >60% by weight, >65% by weight or >70% by weight, >75% by weight, >80% by weight, >85% by weight or >90% by weight.

[0054] The content of the optionally stabilised ceria can be >5% by weight, >10% by weight, >15% by weight, >20% by weight, >30% by weight, >35% by weight, >40% by weight, >45% by weight, >50% by weight, >55% by weight, >60% by weight, >65% by weight or >70% by weight.

[0055] The content of the inorganic fibres can be >5% by weight, >10% by weight, >15% by weight or >20% by weight.

[0056] In an embodiment particularly suited for a catalyst for reducing oxides of nitrogen using a nitrogenous reductant the extruded solid body consists essentially of: 10-95% by weight of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, a spinel, an optionally doped alumina, a source of silica, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof; 50-90% by weight of a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof, each optionally containing one or more metal; and 0-25% by weight of inorganic fibres. This extruded solid body is used to make a wall-flow filter. Preferred embodiments contain inorganic fibres.

[0057] According to a further embodiment, the wall-flow filter extruded solid body consists essentially of 10-95% by weight of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, alumina, a spinel, a silica source, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof; 5-50% by weight of the zeolitic molecular sieve, the non-zeolitic molecular sieve or the mixture of any two or more thereof; 20-80% by weight ceria; and 0-25% by weight of inorganic fibres.

[0058] Further embodiments can use an extruded solid body consisting essentially of: 10-37% by weight of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, an optionally doped alumina, a spinel, a silica source, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof; 60-88% by weight of a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof, each optionally containing one or more metal; and 0-20% by weight of inorganic fibres; or: 15-30% by weight of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, an optionally doped alumina, a spinel, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof; 2-20% by weight of a source of silica; 50-81% by weight of a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof, each optionally containing one or more metal; and 2-10% by weight of inorganic fibres.

[0059] In another embodiment the extruded solid body can consist essentially of: 10-95% by weight of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, an optionally doped alumina, a spinel, a silica source, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof; 0-50% by weight of a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof, each optionally containing one or more metal; 20-80% by weight optionally stabilised ceria; and 0-25% by weight of inorganic fibres. Preferred embodiments contain zeolites and inorganic fibres.

[0060] In developing extruded solid bodies for use in NO_x trap catalysts according to the present invention, we have encountered a lack of strength in the extruded solid body in the composition: 69% by weight of CeO_2, and 23% by weight of γ-Al_2O_3 and 8% by weight glass fibres. Current proposals for increasing strength include pre-calcining the CeO_2 material to reduce surface loss during calcinations of the "green" extruded solid body; increasing the alumina content to 50%+; changing the particle size of the alumina (e.g. from commercially available Pural™ to Disperal™) and/or the optionally stabilised ceria; adding an inert binder to increase mechanical stability e.g. a clay; use a different alumina e.g. an alumina sol; testing other binder systems e.g. TiO_2 sols, CeO_2 sols; cerium acetate; zirconium acetate; optimising the pH; and adding surface modifiers e.g. aluminium salts or other organic surfactants. However, in one embodiment

the content of a source of silica will be reduced or removed altogether.

[0061] The porosity of the extruded bodies for transforming into wall-flow filters can be from 30-80%, such as from 40-70%. A desirable feature of the extruded solid bodies for use in the present invention is that they have good pore interconnectivity and as few closed or "dead end" pores as possible. Suitable mean pore diameters are from 8-25 μm, such as from 15-20 μm. The porosity values expressed herein can be measured by mercury porosimetry or electron microscopy.

[0062] In a more specific example according to the present invention a wall-flow filter for converting oxides of nitrogen in the presence of a reducing agent comprises an extruded solid body consisting essentially of: 10-95% by weight of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, a spinel, an optionally doped alumina, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof; 0-30% by weight of a source of silica; 50-90% by weight of a non-zeolitic molecular sieve containing 1-20% by weight of one or more metal selected from the group consisting of Cu, Fe and Ce; and 0-20% by weight of inorganic fibres.

[0063] According to a further aspect, the invention provides a process of manufacturing a wall-flow filter according to the invention comprising the steps of: forming a solid extruded body by mixing powdered starting materials of: at least one binder/matrix component or a precursor of one or more thereof; optional zeolitic molecular sieve, non zeolitic molecular sieve or a mixture of any two or more thereof which zeolitic molecular sieve, non-zeolitic molecular sieve or mixture of zeolitic and non-zeolitic molecular sieves being optionally associated with at least one metal; an optional optionally stabilised ceria with optional inorganic fibres; and at least one metal compound; optionally adding an organic auxiliary agent; processing by mixing and/or kneading in an acid or alkaline aqueous solution optionally containing a metal salt of at least one metal into a plastic compound to form a mixture; extruding the mixture into a catalyst body, drying the catalyst body and calcining to form a solid extruded body; selecting quantitative proportions of the starting materials such that the solid extruded body contains 10-95% by weight of at least one binder/matrix component; 5-90% by weight of a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof; and 0-80% by weight optionally stabilised ceria, and at least one metal or metal compound and impregnating a surface of the solid extruded body with at least one metal and/or coating a surface of the solid extruded body with at least one coating layer(s) containing at least one metal.

[0064] Typically, a cement is used impermeably to plug ends of channels in an extruded substrate monolith to form the wall-flow filter, e.g. as is disclosed in EP 1837063.

[0065] Very generally, the production of an extruded solid body, a binder, an organic viscosity-enhancing compound and a liquid for converting the material by blending into an homogeneous paste are added to the binder/matrix component or a precursor thereof and optional molecular sieve, optional optionally stabilised ceria, optional inorganic fibres and optional at least one metal compound, and the mixture is compacted in a mixing or kneading apparatus or an extruder. The mixtures have organic additives such as binders, plasticizers, surfactants, lubricants, dispersants as processing aids to enhance wetting and therefore produce a uniform batch. The resulting plastic material is then moulded, in particular using an extrusion press or an extruder including an extrusion die, and the resulting mouldings are dried and calcined. The organic additives are "burnt out" during calcinations of the extruded solid body.

[0066] The at least one binder/matrix component is selected from the group consisting of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, a spinel, an optionally doped alumina, a silica source, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof. An alumina precursor can be used which is aluminium hydroxide or boehmite. Where an aluminium oxide is used, to ensure the binding with the aluminium oxide, it is advantageous to add an aqueous solution of a water-soluble metal salt to the aluminium oxide or the precursor substance of the aluminium oxide before adding the other starting materials.

[0067] In embodiments, the silica source can be selected from the group consisting of a silica, a silica sol, quartz, fused or amorphous silica, sodium silicate, an amorphous aluminosilicate, an alkoxysilane, a silicone resin binder, a clay, talc or a mixture of any two or more thereof.

[0068] In a particular embodiment, the silica source is a silicone resin binder and a solvent for the silicone resin binder is isopropyl alcohol or a dibasic ester.

[0069] One embodiment of the process according to the present invention comprises the step of first admixing an optionally doped alumina or a precursor thereof with the solution and subsequently admixing the zeolitic molecular sieve, non zeolitic molecular sieve or a mixture of any two or more thereof and the inorganic fibres.

[0070] The organic auxiliary agent for use in the process according to the present invention can be one or more selected from the group consisting of a cellulose derivative, an organic plasticizer, a lubricant and a water-soluble resin. Examples of suitable cellulose derivatives include cellulose ethers selected from the group consisting of methylcellulose, ethylcellulose, carboxymethylcellulose, ethylhydroxyethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, methylhydroxyethylcellulose, methylhydroxypropylcellulose and combinations of any two or more thereof. Cellulose derivatives increase the porosity of the final product, which is advantageous for the catalytic activity of the solid catalyst body. Initially the cellulose swells in the aqueous suspension but is ultimately removed during the calcining process.

[0071] The organic plasticizer for use in the process of the present invention is selected from the group consisting of

polyvinyl alcohol, polyvinyl butyral, an ionomer, acrylics, copolyethylene/acrylic acid, polyurethane, a thermoplastic elastomers, a relatively low molecular weight polyester, linseed oil, a ricinoleate and combinations of any two or more thereof.

[0072] The water-soluble resin can be a polyacrylate.

[0073] The lubricant for use in the process according to the present invention is selected from at least one of the group consisting of ethylene glycol, stearic acid, sodium stearate, glycerine and glycols.

[0074] Depending on the composition of the extrudate composition, the pH can be acid or alkaline. Where the process uses an acidic aqueous solution, the pH-value of the solution can be between 3 and 4. Desirably, acetic acid is used to acidify the solution.

[0075] Where the process uses an alkaline aqueous solution, the pH-value of the solution can be between 8 and 9. Ammonia can be used to adjust the pH to the alkaline side.

[0076] According to a further aspect, the invention provides a method of treating exhaust gas emissions from internal combustion engines comprising particulate matter and oxides of nitrogen from a stationary source or a vehicle, which method comprising contacting the exhaust gas mixed with a nitrogenous reductant with a filtering surface of the wall-flow filter according to the invention. In one embodiment, nitric oxide in the oxides of nitrogen is oxidised to nitrogen dioxide upstream of the filtering surface of the wall-flow filter. A temperature at which the exhaust gas contacts the catalyst is preferably >100°C, such as >150°C, >175°C, >200°C, >225°C, >250°C, >275°C or >300°C. Preferably, the temperature at which the exhaust gas contacts the catalyst is <600°C, such as <550°C, <525°C or <500°C.

[0077] According to a further aspect, the invention provides an exhaust system for an internal combustion engine, which exhaust system comprising a wall-flow filter according to the invention, a source of nitrogenous reductant and means for injecting nitrogenous reductant into a flowing exhaust gas upstream of the wall-flow filter. In a preferred embodiment, an oxidation catalyst for oxidising nitrogen oxide to nitrogen dioxide is disposed in the exhaust system upstream of the means for injecting nitrogenous reductant into a flowing exhaust gas.

[0078] In another aspect according to the invention there is provided a vehicle, e.g. an automobile, comprising an internal combustion engine and an exhaust system according to the invention. The internal combustion engine can be a compression ignition engine or a positive ignition engine. A positive ignition engine is typically fuelled with gasoline fuel, but other fuels can be used including gasoline fuel blended with oxygenates including methanol and/or ethanol, liquid petroleum gas or compressed natural gas. Compression ignition engines can be fuelled by diesel fuel, blends of diesel fuel and biodiesel or Fischer-Tropsch derived fuels, biodiesel as such or natural gas as such. Modem compression ignition engines including those known as the Dilution Controlled Combustion System (DCCS), for example Toyota®'s Smoke-less Rich Combustion concept. Emissions from Homogeneous Charge Compression Ignition (HCCI) engines may also be treated. In particular, modern engines wherein substantially all fuel for combustion is injected into a combustion chamber prior to the start of combustion may be treated. In a preferred embodiment, the internal combustion engine is a compression ignition engine.

[0079] In order that the invention may be more fully understood, the following Examples are provided by way of illustration only and with reference to the accompanying drawings in which:

Figure 1 is a graph comparing the pore volume and porosity of various V_2O_5/WO_x-TiO_2 filter materials prepared using various pore modifiers relative to a Reference product used in a flow-through configuration; and

Figure 2 is a graph plotting the pore volume against pore radius for a number of pore modifiers relative to the V_2O_5/WO_x-TiO_2 Reference and a commercially available wallflow filter substrate.

EXAMPLE 1 - EXTRUDED V_2O_5/WO_x-TiO_2 FILTER

[0080] A Reference extruded V_2O_5/WO_x-TiO_2 solid body was prepared by blending components A, B, F and S as set out in Table 1 with water to make a kneadable paste. Additives H (pore modifiers) were added and the material was kneaded for 10 mins to disperse the pore modifiers. The resulting composition was extruded, dried and calcined. It should be noted that the percentage quantities of inorganic solids present in the final calcined article is 100%. Quantities of additives (here H and S) that are removed by combustion during calcination are provided in wt% relative to the 100% inorganic solids content.

Table 1

Active Components		Binder			Stabilizer	Extrusion Additive			Additional Additives		
A1	A2	B1	B2	B3	F1	H1	H2	H3	S1	S2	S3

(continued)

Active Components		Binder			Stabilizer	Extrusion Additive			Additional Additives		
82,90	1,70	3,00	3,00	1,40	8,00	1,00	1,00	0,30	1,76	9,20	0,56
A1 = TiW (98,9%, MC 10/Cristal) A2 = V_2O_5 from AMV (78% V_2O_5, GFE) B1 = Bentonite (90%, ACE/Mizuka) B2 = Kaolin (97,9% TK0177/Thiele) B3 = SiO_2 (100%, Tixosil/Novus) F1 = Glass fibres (Vetrotex 4,5 mm/Saint Gobain) H1 = Cellulose (QP10000H/Nordmann) H2 = PEO (Alkox/Alroko) H3 = Zusoplast (Zschimmer & Schwarz) S1 = MEA (Imhoff & Stahl) S2 = NH_3 S3 = 2-Hydroxy-propanoic-acid (Lactic acid; $C_3H_6O_3$) (Fauth)											

[0081] The following pore modifiers were used instead of the Extrusion Additives H1, H2 and H3 in Table 1, with amounts shown being relative to the total weight of inorganic solid in the recipe of Table 1.

Table 2

Pore Modifier	Wt% Used in Table 1 Recipe	Pore Volume (mm^3/g)	Pore Radius (Å)	Porosity (%)
Reference	See Table 1	310.1	1783.6	39.8
Cellulose CMC-QP10000H (Nordmann)	20			
BC200 (Kremer Pigmente GmbH & Co. KG)	13			
PAN Fibres	13			
Recycling	9	333.6	1930.9	41.2
Arbocel (Schwarzwälder Textil-Werke)	10	427	2950	47.2
HOP Fibre (Osthoff-Petrasch GmbH)	10	426	2629	48.8
Arbocel (Schwarzwälder Textil-Werke)	15	524	5281	50.2
HOP Fibre (Osthoff-Petrasch GmbH)	15	543	3085	54.4

[0082] Porosity and pore volume and pore radius can be measured e.g. using mercury intrusion porosimetry.

[0083] The results of Table 2 entries including pore volume and porosity are also represented in Figure 1. It can be seen from these results that the porosity and pore volume of the Reference can be increased by appropriate selection of pore modifiers so that an extruded solid body made using such pore modifiers may be used in the manufacture of wall-flow filters.

[0084] These results are generic for increasing the porosity, pore volume etc. properties independent of the active components of the solid extruded body. That is, although increasing porosity and pore volume etc. of this Example 1 are illustrated using V_2O_5/WO_x-TiO_2 active materials, the principles of increasing porosity and pore volume etc. disclosed in this Example 1 are applicable to the extrusion of any active material, e.g. an extruded solid body for use in a gasoline soot filter comprising a three-way catalyst, because the pore modifiers are burnt out in the calcination process leaving the active materials and fillers etc. behind as inorganic solids.

[0085] Figure 2 compares the pore volume of a different Reference with solid extruded V_2O_5/WO_x-TiO_2 materials prepared using other pore modifiers set out in Table 2 compared also with a commercially available wallflow filter (NGK®). It can be seen from the graph that the inclusion of pore modifiers has improved the porosity and pore volume of the Reference extruded solid body so that the materials have properties approaching those of commercially available wall-

flow filters.

EXAMPLE 2 - EXTRUDED ZEOLITE MONOLITH SUBSTRATE

[0086] An extruded zeolite monolith substrate was made according to methods similar to those disclosed in US 7,507,684. Powdered commercially available beta zeolite in hydrogen form is mixed with glass fibres, Kaolin filler and powdered synthetic boehmite (Pural SB®) and is processed in an aqueous solution with a pH-value of 5-6 into a shapeable and flowable slip by admixture with cellulose (CMC-QP10000H), the plasticizer Zusoplast (a brand name of Zschimmer & Schwarz GmbH & Co KG) and the organic auxiliary agent PEO Alkox (a polyethylene oxide) in quantities selected using Example 1 as a guide to provide a desired level of porosity. The quantitative proportions of the starting materials are selected in such a way that the active material of the finished solid catalyst body contains 69% by weight of zeolite, 23% by weight of γ-Al_2O_3, 5% by weight of glass fibres and 3% by weight of Kaolin. The shapeable mixture is extruded into a flowthrough honeycomb catalyst body, i.e. with continuous channels and with a circular cross-section exhibiting a cell density of 300 cpsi (46.5 cells cm^{-2}) or 400 cpsi (cells per square inch) (62 cells cm^{-2}). Subsequently, the catalyst body is freeze dried for 1 hour at 2mbar (200 Pa) according to the method described in WO 2009/080155 and calcined at a temperature of 580°C to form a solid catalyst body.

EXAMPLE 3 - EXTRUDED ZEOLITE MONOLITH SUBSTRATE CONTAINING FE-BETA ZEOLITE

[0087] Powdered commercially available beta zeolite in hydrogen form is mixed with iron hydroxide, glass fibres, a low alkaline clay filler and powdered synthetic boehmite (Pural SB®) and is processed in an aqueous solution with a pH-value of 5-6 into a shapeable and flowable slip. When the mixture is well plasticised, cellulose is added at 8wt% based on 100% of the total inorganic solids content. The quantitative proportions of the starting materials are selected in such a way that the active material of the finished solid catalyst body contains 55% by weight of zeolite, 25% by weight of the clay, 7% by weight of γ-Al_2O_3, 8% by weight of glass fibres and 5% by weight of iron and iron compounds in quantities selected using Example 1 as a guide to provide a desired level of porosity. The shapeable mixture is extruded into a flow-through honeycomb catalyst body, i.e. with continuous channels and with a circular cross-section exhibiting a cell density of 400 cpsi (cells per square inch) (62 cells cm^{-2}). Subsequently, the catalyst body is freeze dried for 1 hour at 2mbar (200 Pa) according to the method described in WO 2009/080155 and reductively calcined according to the method described WO2011/026573A1 at a temperature of 580°C to form a solid catalyst body. It is found that by using the method described that at least some of the iron introduced into the mixture becomes ion-exchanged with the zeolite.

EXAMPLE 4 - EXTRUDED WALL-FLOW SCR FILTER

[0088] This is a prophetic example. A wall-flow filter monolith substrate similar to WO 2009/093071 can be prepared as follows. An extruded monolith substrate comprising a non-zeolitic molecular sieve may be made according to methods similar to those disclosed in US 7,507,684 and Example 1. An ion-exchanged SAPO-34, the active material of which contains 3% by weight of copper, may be mixed with glass fibres and powdered synthetic boehmite (Pural SB®) and processed in an aqueous solution with a pH-value of 3.5 into a shapeable and flowable slip containing a wt% of 3.5wt% cellulose (CMC-QP10000H), 1.8wt% of the plasticizer Zusoplast (a brand name of Zschimmer & Schwarz GmbH & Co KG) 3.5wt% of the organic auxiliary agent PEO Alkox (a polyethylene oxide) and a total of 13wt% of a mixture of the pore modifiers Rettenmaier BC200, a natural cellulosic material and polyacrylonitrile (PAN) fibres. The quantitative proportions of the starting materials may be selected in such a way that the active material of the finished solid catalyst body contains 60% by weight of Cu-exchanged SAPO-34, 35% by weight of γ-Al_2O_3, 5% by weight of glass fibres. The shapeable mixture may be extruded into a honeycomb catalyst body with continuous channels and with a circular cross-section exhibiting a cell density of 300 cpsi (cells per square inch) (46.5 cells cm^{-2}). Subsequently, the catalyst body may be freeze dried for 1 hour at 2mbar (200 Pa) according to the method described in WO 2009/080155 and calcined at a temperature of 580°C to form a solid catalyst body. The extruded zeolite monolith substrate is expected to have an inflow area with a diameter of approximately 14 cm and a flow-through length of approximately 19 cm. The resulting product typically would have a mean pore size of approximately 10μm.

[0089] The extruded flow-through monolith substrate comprising a plurality of channels may be made into a wall-flow filter arrangement whereby a plurality of first channels is plugged at an upstream end and a plurality of second channels not plugged at the upstream end are plugged at a downstream end, wherein the arrangement of the first and second channels is such that laterally and vertically adjacent channels are plugged at opposite ends in the appearance of a checkerboard by inserting substantially gas impermeable plugs at the ends of the channels in the desired pattern according to EP 1837063. This filter arrangement is also disclosed in SAE 810114.

[0090] The wall-flow filter can be coated with a washcoat according to the methods disclosed in WO 99/47260 or WO2011080525A1. The latter method comprises the steps of: (i) holding a honeycomb monolith substrate substantially

vertically; (ii) introducing a pre-determined volume of the liquid into the substrate via open ends of the channels at a lower end of the substrate; (iii) sealingly retaining the introduced liquid within the substrate; (iv) inverting the substrate containing the retained liquid; and (v) applying a vacuum to open ends of the channels of the substrate at the inverted, lower end of the substrate to draw the liquid along the channels of the substrate.

Claims

1. A wall-flow filter comprising a catalyst for converting oxides of nitrogen in the presence of a reducing agent, which wall-flow filter comprising an extruded solid body comprising:

   10-95% by weight of at least one binder/matrix component;
   5-90% by weight of a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof; and
   0-80% by weight optionally stabilised ceria,
   which catalyst comprising at least one metal, wherein:

   (i) the at least one metal is present throughout the extruded solid body and is also present in a higher concentration at a surface of the extruded solid body;
   (ii) the at least one metal is present throughout the extruded solid body and is also carried in one or more coating layer(s) on a surface of the extruded solid body; or
   (iii) the at least one metal is present throughout the extruded solid body, is present in a higher concentration at a surface of the extruded solid body and is also carried in one or more coating layer(s) on the surface of the extruded solid body.

2. A wall-flow filter according to claim 1, wherein the extruded solid body comprises:

   10-95% by weight of a cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, an optionally doped alumina, a silica source, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof;
   0-80% by weight of spinel;
   5-90% by weight of a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof, each optionally containing one or more metal;
   0-80% by weight optionally stabilised ceria; and
   0-25% by weight inorganic fibres.

3. A wall-flow filter according to claim 1 or 2, wherein the porosity of the wall-flow filter is from 30-80%.

4. A wall-flow filter according to any preceding claim comprising a zeolitic molecular sieve or a non-zeolitic molecular sieve, wherein the zeolitic molecular sieve or a non-zeolitic molecular sieve has the framework type code ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOF, BOG, BPH, BRE, BSV, CAN, CAS, CDO, CFI, CGF, CGS, CHA, -CHI, -CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EON, EPI, ERI, ESV, ETR, EUO, EZT, FAR, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, IHW, IMF, ISV, ITE, ITH, ITR, ITW, IWR, IWS, IWV, IWW, JBW, JRY, KFI, LAU, LEV, LIO, -LIT, LOS, LOV, LTA, LTF, LTL, LTN, MAR, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MOZ, MRE, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NES, NON, NPO, NSI, OBW, OFF, OSI, OSO, OWE, -PAR, PAU, PHI, PON, RHO, -RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBN, SBS, SBT, SFE, SFF, SFG, SFH, SFN, SFO, SFS, SGT, SIV, SOD, SOF, SOS, SSF, SSY, STF, STI, STO, STT, STW, -SVR, SZR, TER, THO, TOL, TON, TSC, TUN, UEI, UFI, UOS, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, -WEN, YUG, ZON as defined by the Structure Commission of the International Zeolite Association and mixtures of any two or more thereof.

5. A wall-flow filter according to claim 4, wherein the zeolitic molecular sieve or the non-zeolitic molecular sieve has a maximum 8-ring pore opening structure as defined by the Structure Commission of the International Zeolite Association.

6. A wall-flow filter according to any preceding claim, wherein the at least one metal present in each of: (a) throughout the extruded solid body; (b) present in a higher concentration at a surface of the extruded solid body; and (c) carried in one or more coating layer(s) on a surface of the extruded solid body in features (i), (ii) and (iii) is different from

the at least one metal present in the other location(s).

7. A wall-flow filter according to any preceding claim comprising a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof, wherein the at least one metal is associated with the zeolitic molecular sieve component, the non-zeolitic molecular sieve component or either or both of the zeolitic molecular sieve component and the non-zeolitic molecular sieve components in the mixture.

8. A wall-flow filter according to claim 7, wherein the or each at least one metal associated with the zeolitic molecular sieve, non-zeolitic molecular sieve or both molecular sieves in the mixture of any two or more thereof, containing one or more metal selected from the group consisting of a transition metal, a lanthanide or a mixture of any two or more thereof.

9. A wall-flow filter according to claim 8, wherein the transition metal is selected from the group consisting of a Group IB metal, a Group IVB metal, a Group VB metal, a Group VIIB metal and a Group VIII metal.

10. A wall-flow filter according to claim 8 or 9, wherein the transition metal is selected from the group consisting of Fe, Cu, Ce, Hf, La, Mn, Pt, Au, Ag, In, Rh, V, Ir, Ru, and Os.

11. A wall-flow filter according to any preceding claim, which filter comprising an extruded solid body consisting essentially of:

10-95% by weight of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, a spinel, an optionally doped alumina, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof;
0-30% by weight of a source of silica;
50-90% by weight of a non-zeolitic molecular sieve containing 1-20% by weight of one or more metal selected from the group consisting of Cu, Fe and Ce; and
0-20% by weight of inorganic fibres.

12. A wall-flow filter according to any preceding claim, wherein the at least one binder/matrix component is selected from the group consisting of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, a spinel, an optionally doped alumina, a silica source, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof.

13. A process of manufacturing a wall-flow filter according to any preceding claim, which process comprising the steps of:

forming a solid extruded body by mixing powdered starting materials of: at least one matrix component or a precursor of one or more thereof; zeolitic molecular sieve, non zeolitic molecular sieve or a mixture of any two or more thereof, which zeolitic molecular sieve, non-zeolitic molecular sieve or mixture of zeolitic and non-zeolitic molecular sieves being optionally associated with at least one metal; an optional optionally stabilised ceria;
and at least one metal compound; with optional inorganic fibres; optionally adding an organic auxiliary agent;
processing by mixing and/or kneading in an acid or alkaline aqueous solution optionally containing a metal salt of at least one metal into a plastic compound to form a mixture;
extruding the mixture into a catalyst body, drying the catalyst body and calcining to form a solid extruded body;
selecting quantitative proportions of the starting materials such that the solid extruded body contains 10-95% by weight of at least one matrix component; 5-90% by weight of a zeolitic molecular sieve, a non-zeolitic molecular sieve or a mixture of any two or more thereof; and 0-80% by weight optionally stabilised ceria, and at least one metal or metal compound and impregnating a surface of the solid extruded body with at least one metal and/or coating a surface of the solid extruded body with at least one coating layer(s) containing at least one metal.

14. A method of treating exhaust gas emissions from internal combustion engines from a stationary source or a vehicle, which method comprising contacting the exhaust gas mixed with a nitrogenous reductant with a wall-flow filter according to any of claims 1 to 12.

15. An exhaust system for an internal combustion engine, which exhaust system comprising a wall-flow filter according to any of claims 1 to 12, a source of nitrogenous reductant and means for injecting nitrogenous reductant into a flowing exhaust gas upstream of the wall-flow filter.

16. A vehicle comprising an internal combustion engine and an exhaust system according to claim 15.

Patentansprüche

1. Wandstromfilter, der einen Katalysator zur Umwandlung von Stickoxiden in Gegenwart eines Reduktionsmittels umfasst, wobei der Wandstromfilter einen extrudierten Festkörper umfasst, welcher Folgendes umfasst:

   10 bis 95 Gewichts-% mindestens eines Bindemittel/Matrix-Bestandteils;
   5 bis 90 Gewichts-% eines zeolithartigen Molekularsieb, eines nichtzeolithartigen Molekularsiebs oder einer Mischung aus zwei oder mehr beliebigen davon; und
   0 bis 80 Gewichts-% an möglicherweise stabilisiertem Cerdioxid,
   wobei der Katalysator mindestens ein Metall umfasst, wobei:

   (i) das mindestens eine Metall in dem gesamten extrudierten Festkörper vorliegt und weiterhin an einer Oberfläche des extrudierten Festkörpers in einer höheren Konzentration vorliegt,
   (ii) das mindestens eine Metall in dem gesamten extrudierten Festkörper vorliegt und weiterhin in einer oder mehreren Beschichtungslage(n) auf einer Oberfläche des extrudierten Festkörpers geträgert vorliegt; oder
   (iii) das mindestens eine Metall in dem gesamten extrudierten Festkörper vorliegt, an einer Oberfläche des extrudierten Festkörpers in einer höheren Konzentration vorliegt und weiterhin in einer oder mehreren Beschichtungslage(n) auf einer Oberfläche des extrudierten Festkörpers geträgert vorliegt;

2. Wandstromfilter nach Anspruch 1, wobei der extrudierte Festkörper Folgendes umfasst:

   10 bis 95 Gewichts-% eines Cordierits, an Nitriden, Carbiden, Boriden, intermetallischen Phasen, Lithiumaluminosilicat, eines möglicherweise dotierten Aluminiumoxids, einer Siliciumdioxidquelle, an Titandioxid, Zirkoniumdioxid, Titandioxid-Zirkoniumdioxid, Zirkon und Mischungen aus zwei oder mehr beliebigen davon;
   0 bis 80 Gewichts-% an Spinell;
   5 bis 90 Gewichts-% eines zeolithartigen Molekularsiebs, eines nichtzeolithartigen Molekularsiebs oder einer Mischung aus zwei oder mehr beliebigen davon, wobei jedes davon möglicherweise ein oder mehrere Metall(e) enthält;
   0 bis 80 Gewichts-% an möglicherweise stabilisiertem Cerdioxid; und
   0 bis 25 Gewichts-% an anorganischen Fasern.

3. Wandstromfilter nach Anspruch 1 oder 2, wobei der Wandstromfilter eine Porosität von 30 bis 80 % aufweist.

4. Wandstromfilter nach einem beliebigen vorhergehenden Anspruch, wobei er ein zeolithartiges Molekularsieb oder ein nicht-zeolithartiges Molekularsieb umfasst, wobei das zeolithartige Molekularsieb oder ein nicht-zeolithartiges Molekularsieb die Gerüststruktur-Kurzbezeichnung ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOF, BOG, BPH, BRE, BSV, CAN, CAS, CDO, CFI, CGF, CGS, CHA, -CHI, - CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EON, EPI, ERI, ESV, ETR, EUO, EZT, FAR, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, IHW, IMF, ISV, ITE, ITH, ITR, ITW, IWR, IWS, IWV, IWW, JBW, JRY, KFI, LAU, LEV, LIO, -LIT, LOS, LOV, LTA, LTF, LTL, LTN, MAR, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MOZ, MRE, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NES, NON, NPO, NSI, OBW, OFF, OSI, OSO, OWE, -PAR, PAU, PHI, PON, RHO, -RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBN, SBS, SBT, SFE, SFF, SFG, SFH, SFN, SFO, SFS, SGT, SIV, SOD, SOF, SOS, SSF, SSY, STF, STI, STO, STT, STW, -SVR, SZR, TER, THO, TOL, TON, TSC, TUN, UEI, UFI, UOS, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, -WEN, YUG, ZON gemäß den Begriffsbestimmungen der internationalen Zeolithvereinigung und Mischungen aus zwei oder mehr beliebigen davon aufweist.

5. Wandstromfilter nach Anspruch 4, wobei das zeolithartige Molekularsieb oder nicht-zeolithartige Molekularsieb eine Porenöffnung aufweist, die nach der Begriffsbestimmung der Internationalen Zeolithvereinigung höchstens einem 8-Ring entspricht.

6. Wandstromfilter nach einem beliebigen vorhergehenden Anspruch, wobei das mindestens eine Metall, welches in jedem der folgenden Bereiche vorliegt: (a) im gesamten extrudierten Festkörper; (b) in einer höheren Konzentration

an einer Oberfläche des extrudierten Festkörpers; und (c) geträgert in einer oder mehreren Beschichtungslage(n) auf einer Oberfläche des extrudierten Festkörpers gemäß den Eigenschaftsmerkmalen (i), (ii) und (iii), sich von dem mindestens einen Metall unterscheidet, welches in dem/den anderen Bereiche(n) vorliegt.

7. Wandstromfilter nach einem beliebigen vorhergehenden Anspruch, wobei es ein zeolithartiges Molekularsieb, ein nicht-zeolithartiges Molekularsieb oder eine Mischung aus zwei oder mehr beliebigen davon umfasst, wobei das mindestens eine Metall innerhalb der Mischung in Verbindung mit dem zeolithartigen Molekularsieb-Bestandteil, dem nicht-zeolithartigen Molekularsieb-Bestandteil oder einem oder beiden der Bestandteile zeolithartiges Molekularsieb und nicht-zeolithartiges Molekularsieb vorliegt.

8. Wandstromfilter nach Anspruch 7, wobei das oder jedes der Metalle, von denen mindestens eines vorliegt und welches innerhalb der Mischung Verbindung mit dem zeolithartigen Molekularsieb, dem nicht-zeolithartigen Molekularsieb oder beiden Molekularsieben vorliegt, ein oder mehrere Metalle enthält, die aus der Gruppe ausgewählt ist/sind, welche aus einem Übergangsmetall, einem Lanthanid oder einer Mischung aus zwei oder mehr beliebigen davon besteht.

9. Wandstromfilter nach Anspruch 8, wobei das Übergangsmetall aus der Gruppe ausgewählt ist, die aus einem Metall der Gruppe IB, einem Metall der Gruppe IVB, einem Metall der Gruppe VB, einem Metall der Gruppe VIIB und einem Metall der Gruppe VIII besteht.

10. Wandstromfilter nach Anspruch 8 oder 9, wobei das Übergangsmetall aus der Gruppe ausgewählt ist, die aus Fe, Cu, Ce, Hf, La, Mn, Pt, Au, Ag, In, Rh, V, Ir, Ru und Os besteht.

11. Wandstromfilter nach einem beliebigen vorhergehenden Anspruch, wobei der Filter einen extrudierten Festkörper umfasst, der im Wesentlichen aus Folgendem besteht:

    10 bis 95 Gewichts-% eines Cordierits, an Nitriden, Carbiden, Boriden, intermetallischen Phasen, Lithiumaluminosilicat, eines Spinells, eines möglicherweise dotierten Aluminiumoxids, an Titandioxid, Zirkoniumdioxid, Titandioxid-Zirkoniumdioxid, Zirkon und Mischungen aus zwei oder mehr beliebigen davon;
    0 bis 30 Gewichts% einer Siliciumdioxidquelle;
    50 bis 90 Gewichts-% eines nicht-zeolithartigen Molekularsiebs, das 1 bis 20 Gewichts-% an einem oder mehreren Metall(en) enthält, das/die aus der Gruppe ausgewählt ist/sind, welche aus Cu, Fe und Ce besteht; und
    0 bis 20 Gewichts-% an anorganischen Fasern.

12. Wandstromfilter nach einem beliebigen vorhergehenden Anspruch, wobei der mindestens eine Bindemittel/Matrix-Bestandteil aus der Gruppe ausgewählt ist, die aus Cordierit, Nitriden, Carbiden, Boriden, intermetallischen Phasen, Lithiumaluminosilicat, einem Spinell, einem möglicherweise dotierten Aluminiumoxid, einer Siliciumdioxidquelle, Titandioxid, Zirkoniumdioxid, Titandioxid-Zirkoniumdioxid, Zirkon und Mischungen aus zwei oder mehr beliebigen davon besteht.

13. Verfahren zur Herstellung eines Wandstromfilters nach einem beliebigen vorhergehenden Anspruch, wobei das Verfahren die folgenden Schritte umfasst:

    Bilden eines feststofflichen extrudierten Körpers, indem die folgenden pulverförmigen Ausgangsmaterialien vermischt werden: mindestens ein Matrix-Bestandteil oder eine Vorläufersubstanz eines oder mehrerer davon; zeolithartiges Molekularsieb, nicht-zeolithartiges Molekularsieb oder eine Mischung aus zwei oder mehr beliebigen davon, wobei das zeolithartige Molekularsieb, das nicht-zeolithartige Molekularsieb oder die Mischung aus zeolithartigem und nicht-zeolithartigem Molekularsieb möglicherweise in Verbindung mit mindestens einem Metall vorliegt; möglicherweise ein Cerdioxid, das möglicherweise stabilisiert ist; und mindestens eine Metallverbindung; möglicherweise mit anorganischen Fasern; wobei möglicherweise ein organisches Hilfsmittel zugesetzt wird;
    Verarbeiten zu einer formbaren Vormischung, indem in einer sauren oder alkalischen wässrigen Lösung, die möglicherweise ein Metallsalz mindestens eines Metalls enthält, ein Misch- und/oder Knetvorgang derart durchgeführt wird, dass sich eine Mischung bildet; Extrudieren der Mischung zu einem Katalysatorkörper, Trocknen des Katalysatorkörpers, und Brennen zwecks Bildung eines feststofflichen extrudierten Körpers,
    wobei die mengenmäßigen Anteile der Ausgangsmaterialien derart sind, dass der feststoffliche extrudierte Körper 10 bis 95 Gewichts-% mindestens eines Matrix-Bestandteils; 5 bis 90 Gewichts-% eines zeolithartigen Molekularsiebs, eines nicht-zeolithartigen Molekularsiebs oder einer Mischung aus mindestens zwei oder mehr

beliebigen davon; und 0 bis 80 Gewichts-% an möglicherweise stabilisiertem Cerdioxid enthält sowie mindestens ein Metall oder eine Metallverbindung, und wobei eine Oberfläche des feststofflichen extrudierten Körpers mit mindestens einem Metall durchtränkt wird und/oder eine Oberfläche des feststofflichen extrudierten Körpers mit mindestens einer Beschichtungslage, die mindestens ein Metall enthält/enthalten, beschichtet wird.

14. Verfahren zur Behandlung von Abgasemissionen von Verbrennungsmotoren, die aus einer stationären Quelle oder einem Fahrzeug stammen, wobei das Verfahren das Inkontaktbringen des Abgases, in Mischung mit einem stickstoffhaltigen Reduktionsmittel, mit einem Wandstromfilter nach einem beliebigen der Ansprüche 1 bis 12 umfasst.

15. Abgassystem für einen Verbrennungsmotor, wobei das Abgassystem einen Wandstromfilter nach einem beliebigen der Ansprüche 1 bis 12, eine Quelle eines stickstoffhaltigen Reduktionsmittels sowie Mittel zum Einspritzen des stickstoffhaltigen Reduktionsmittels in ein strömendes Abgas stromaufwärts des Wandstromfilters umfasst.

16. Fahrzeug, das einen Verbrennungsmotor und ein Abgassystem nach Anspruch 15 umfasst.

Revendications

1. Filtre à parois filtrantes comprenant un catalyseur de conversion des oxydes d'azote en présence d'un agent réducteur, lequel filtre à parois filtrantes comprenant un corps solide extrudé comprenant :

10 à 95 % en poids d'au moins un composant formant liant/matrice ;
5 à 90 % en poids d'un tamis moléculaire zéolitique, d'un tamis moléculaire non zéolitique ou d'un mélange de n'importe lesquels de deux ou plusieurs d'entre eux ; et
0 à 80 % en poids d'oxyde de cérium éventuellement stabilisé,
lequel catalyseur comprenant au moins un métal :

(i) le au moins un métal étant présent à travers le corps solide extrudé et étant également présent en une concentration supérieure au niveau d'une surface du corps solide extrudé ;
(ii) le au moins un métal étant présent à travers le corps solide extrudé et étant également porté dans l'une ou plusieurs couche(s) de revêtement sur une surface du corps solide extrudé ; ou
(iii) le au moins un métal étant présent à travers le corps solide extrudé, étant présent en une concentration supérieure au niveau d'une surface du corps solide extrudé et étant également porté dans l'une ou plusieurs couche(s) de revêtement sur la surface du corps solide extrudé.

2. Filtre à parois filtrantes selon la revendication 1, le corps solide extrudé comprenant : 10 à 95 % en poids d'une cordiérite, de nitrures, de carbures, de borures, d'intermétalliques, d'aluminosilicate de lithium, d'une alumine éventuellement dopée, d'une source de silice, d'oxyde de titane, d'oxyde de zirconium, d'oxyde de titane-zirconium, de zircon et de mélanges de n'importe lesquels de deux ou plusieurs d'entre eux ;

0 à 80 % en poids de spinelles ;
5 à 90 % en poids d'un tamis moléculaire zéolitique, d'un tamis moléculaire non zéolitique ou d'un mélange de n'importe lesquels de deux ou plusieurs d'entre eux, contenant chacun éventuellement un ou plusieurs métaux ;
0 à 80 % en poids d'oxyde de cérium éventuellement stabilisé ; et
0 à 25 % en poids de fibres inorganiques.

3. Filtre à parois filtrantes selon la revendication 1 ou 2, la porosité du filtre à parois filtrantes étant de 30 à 80 %.

4. Filtre à parois filtrantes selon l'une quelconque des revendications précédentes comprenant un tamis moléculaire zéolitique ou un tamis moléculaire non zéolitique, le tamis moléculaire zéolitique ou un tamis moléculaire non zéolitique ayant le code de type de réseau ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOF, BOG, BPH, BRE, BSV, CAN, CAS, CDO, CFI, CGF, CGS, CHA, -CHI, -CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EON, EPI, ERI, ESV, ETR, EUO, EZT, FAR, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, IHW, IMF, ISV, ITE, ITH, ITR, ITW, IWR, IWS, IWV, IWW, JBW, JRY, KFI, LAU, LEV, LIO, -LIT, LOS, LOV, LTA, LTF, LTL, LTN, MAR, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MOZ, MRE, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NES, NON, NPO, NSI, OBW, OFF, OSI, OSO, OWE, -PAR, PAU, PHI, PON, RHO, -RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBN, SBS,

SBT, SFE, SFF, SFG, SFH, SFN, SFO, SFS, SGT, SIV, SOD, SOF, SOS, SSF, SSY, STF, STI, STO, STT, STW, -SVR, SZR, TER, THO, TOL, TON, TSC, TUN, UEI, UF1, UOS, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, -WEN, YUG, ZON tel que défini par la Structure Commission de l'International Zeolite Association et les mélanges de n'importe lesquels de deux ou plusieurs d'entre eux.

5. Filtre à parois filtrantes selon la revendication 4, le tamis moléculaire zéolitique ou le tamis moléculaire non zéolitique ayant une structure maximale d'ouverture de pores à 8 anneaux telle que définie par la Commission Structure de l'International Zeolite Association.

6. Filtre à parois filtrantes selon l'une quelconque des revendications précédentes, le au moins un métal étant présent dans chacun de : (a) partout dans le corps solide extrudé ; (b) présent en une concentration supérieure à une surface du corps solide extrudé ; et (c) porté dans l'une ou plusieurs couche(s) de revêtement sur une surface du corps solide extrudé dans les caractéristiques (i), (ii) et (iii) étant différent du au moins un métal présent dans l'(les) autre(s) emplacement(s).

7. Filtre à parois filtrantes selon l'une quelconque des revendications précédentes comprenant un tamis moléculaire zéolitique, un tamis moléculaire non zéolitique ou un mélange de n'importe lesquels de deux ou plusieurs d'entre eux, le au moins un métal étant associé au composant tamis moléculaire zéolitique, au composant tamis moléculaire non zéolitique ou à l'un ou les deux entre le composant tamis moléculaire zéolitique et les composants tamis moléculaires non zéolitiques dans le mélange.

8. Filtre à parois filtrantes selon la revendication 7, le ou chacun d'au moins un métal associé au tamis moléculaire zéolitique, au tamis moléculaire non zéolitique ou aux deux tamis moléculaires dans le mélange de n'importe lesquels de deux ou plusieurs d'entre eux, contenant un ou plusieurs métal(métaux) sélectionné(s) parmi le groupe constitué d'un métal de transition, d'un lanthanide ou d'un mélange de n'importe lesquels de deux ou plusieurs d'entre eux.

9. Filtre à parois filtrantes selon la revendication 8, le métal de transition étant sélectionné parmi le groupe constitué d'un métal du Groupe IB, d'un métal du Groupe IVB, d'un métal du Groupe VB, d'un métal du Groupe VIIB et d'un métal du Groupe VIII.

10. Filtre à parois filtrantes selon la revendication 8 ou 9, le métal de transition étant sélectionné parmi le groupe constitué de Fe, Cu, Ce, Hf, La, Mn, Pt, Au, Ag, In, Rh, V, Ir, Ru, et Os.

11. Filtre à parois filtrantes selon l'une quelconque des revendications précédentes, lequel filtre comprenant un corps solide extrudé constitué essentiellement de :

10 à 95 % en poids de cordiérite, de nitrures, de carbures, de borures, d'intermétalliques, d'aluminosilicate de lithium, de spinelles, d'alumine éventuellement dopée, d'oxyde de titane, d'oxyde de zirconium, d'oxyde de titane-zirconium, de zircon et de mélanges de n'importe lesquels de deux ou plusieurs d'entre eux ;
0 à 30 % en poids d'une source de silice ;
50 à 90 % en poids d'un tamis moléculaire non zéolitique contenant 1 à 20 % en poids d'un ou plusieurs métaux sélectionné(s) parmi le groupe constitué de Cu, Fe et Ce ; et
0 à 20 % en poids de fibres inorganiques.

12. Filtre à parois filtrantes selon l'une quelconque des revendications précédentes, le au moins un composant formant liant/matrice étant sélectionné parmi le groupe constitué de la cordiérite, des nitrures, des carbures, des borures, des intermétalliques, de l'aluminosilicate de lithium, des spinelles, de l'alumine éventuellement dopée, d'une source de silice, d'oxyde de titane, d'oxyde de zirconium, d'oxyde de titane-zirconium, de zircon et de mélanges de n'importe lesquels de deux ou plusieurs d'entre eux.

13. Procédé de fabrication d'un filtre à parois filtrantes selon l'une quelconque des revendications précédentes, lequel procédé comprenant les étapes de :

formation d'un corps solide extrudé par mélange de matières de départ pulvérulentes de : au moins un composant formant matrice ou un précurseur d'un ou plusieurs d'entre eux ; tamis moléculaire zéolitique, tamis moléculaire non zéolitique ou un mélange de n'importe lesquels de deux ou plusieurs d'entre eux, lequel tamis moléculaire zéolitique, tamis moléculaire non zéolitique ou mélange de tamis moléculaires zéolitiques et non zéolitiques étant éventuellement associés à au moins un métal ; un oxyde de cérium facultatif éventuellement stabilisé ;

et au moins un composé métallique ; avec des fibres inorganiques facultatives ; l'addition éventuelle d'un agent auxiliaire organique ;
le traitement par mélange et/ou malaxage dans une solution aqueuse acide ou alcaline contenant éventuellement un sel métallique d'au moins un métal dans un composé plastique pour former un mélange ; l'extrusion du mélange en un corps catalyseur, le séchage du corps catalyseur et la calcination pour former un corps solide extrudé ;
la sélection de proportions quantitatives des matériaux de départ de sorte que le corps solide extrudé contienne 10 à 95 % en poids d'au moins un composant formant matrice ; 5 à 90 % en poids d'un tamis moléculaire zéolitique, d'un tamis moléculaire non zéolitique ou d'un mélange de n'importe lesquels de deux ou plusieurs d'entre eux ; et de 0 à 80 % en poids d'oxyde de cérium éventuellement stabilisé, et au moins un métal ou composé métallique et l'imprégnation d'une surface du corps solide extrudé avec au moins un métal et/ou le revêtement d'une surface du corps solide extrudé avec au moins une couche de revêtement contenant au moins un métal.

14. Procédé de traitement d'émissions de gaz d'échappement provenant de moteurs à combustion interne à partir d'une source stationnaire ou d'un véhicule, lequel procédé comprenant la mise en contact du gaz d'échappement mélangé à un réducteur azoté avec un filtre à parois filtrantes selon l'une quelconque des revendications 1 à 12.

15. Système d'échappement pour moteur à combustion interne, lequel système d'échappement comprenant un filtre à parois filtrantes selon l'une quelconque des revendications 1 à 12, un source d'agent réducteur azoté et un moyen d'injection de l'agent réducteur azoté dans un gaz d'échappement en écoulement situé en amont du filtre à parois filtrantes.

16. Véhicule comprenant un moteur à combustion interne et un système d'échappement selon la revendication 15.

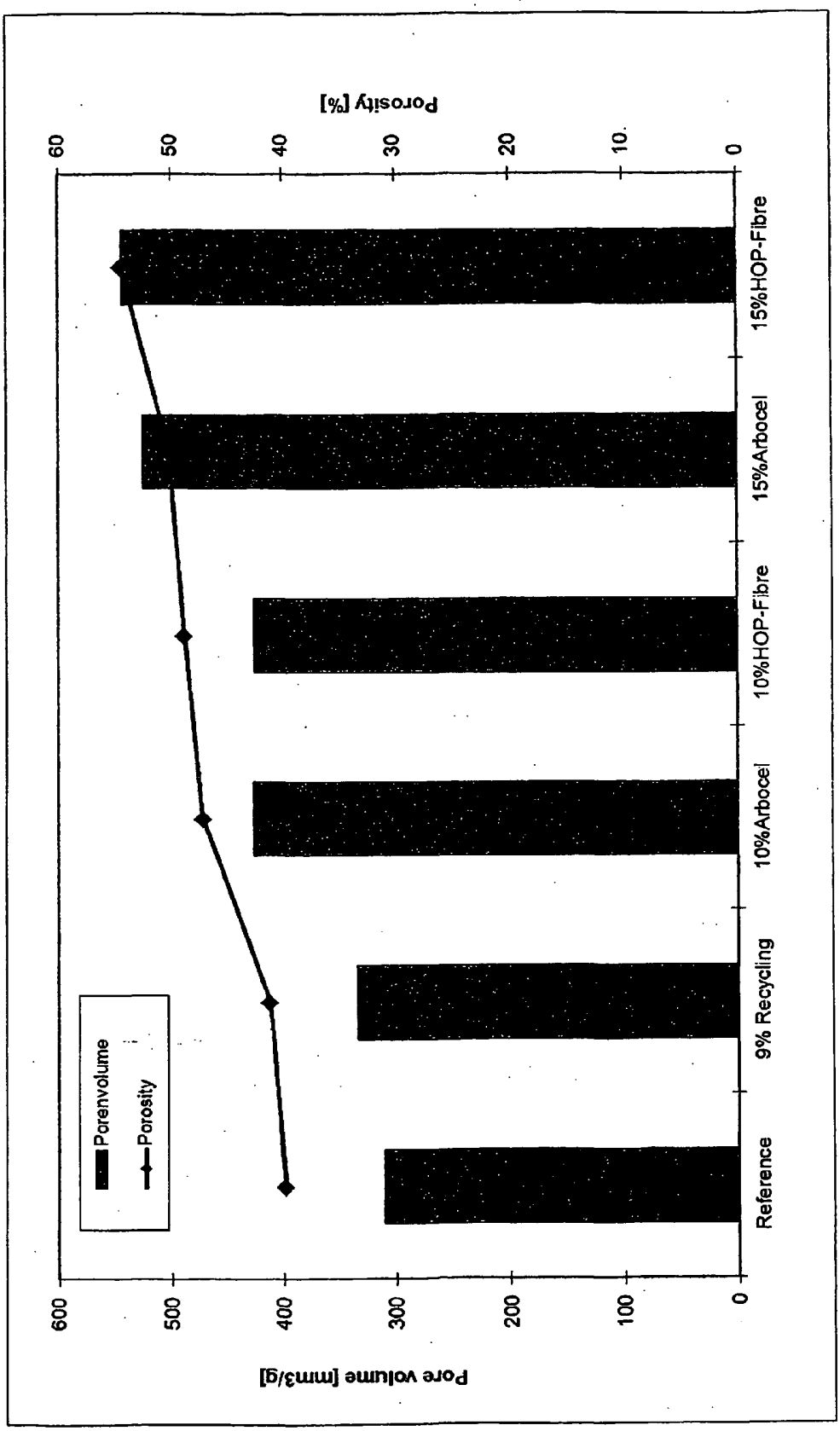
Porosity [%]
60
50
40
30
20
10
0
Pore volume [mm3/g]
600
500
400
300
200
100
0
Parenvolume
Porosity
Reference
9% Recycling
10%Arbocel
10%HOP-Fibre
15%Arbocel
15%HOP-Fibre

FIGURE 1

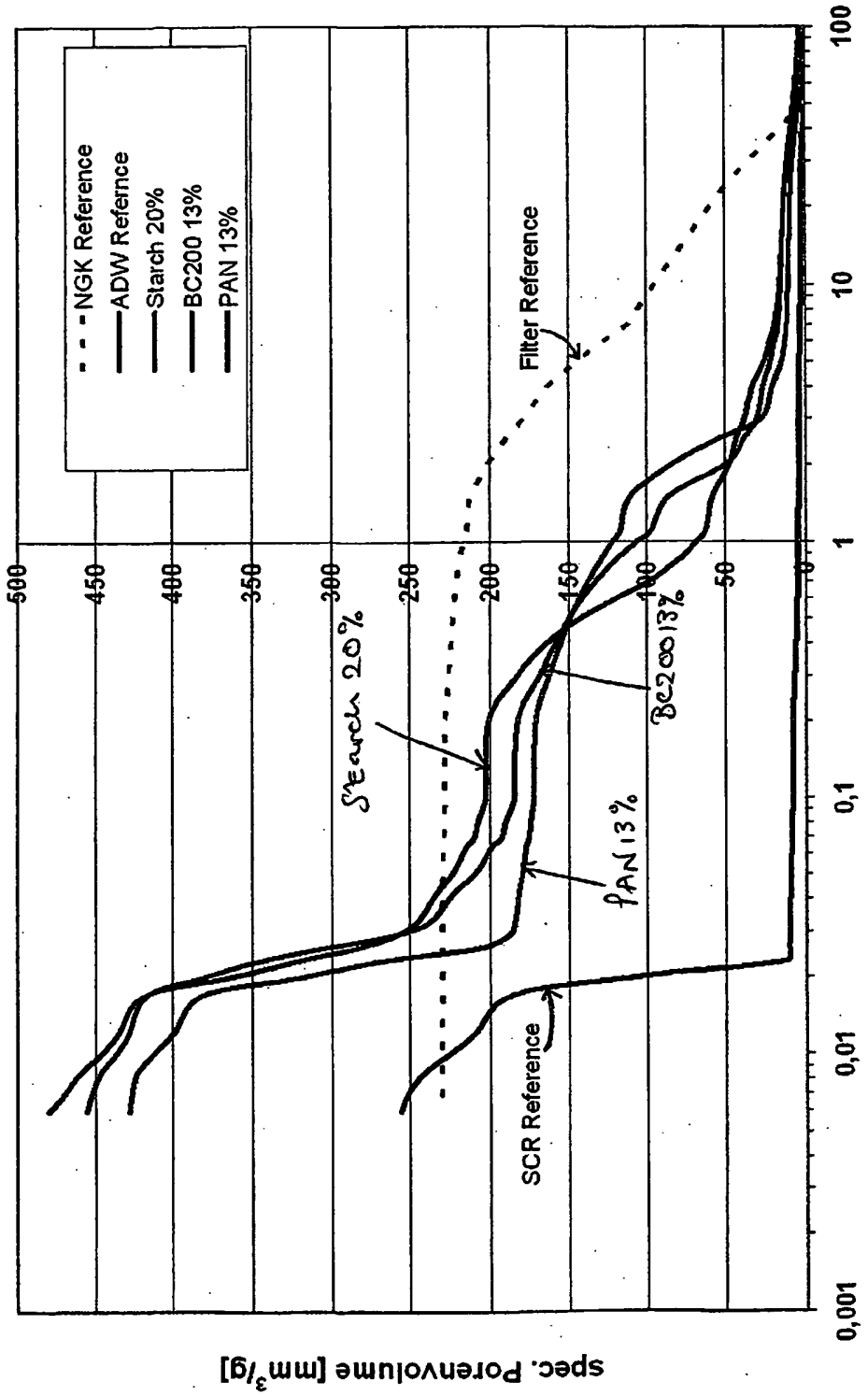
NGK Reference
ADW Reference
Starch 20%
BC200 13%
PAN 13%
Filter Reference
SCR Reference
Starch 20%
BC200 13%
PAN 13%
spec. Porenvolume [mm³/g]
Poreradius [µm]
500
450
400
350
300
250
200
150
100
50
0
0,001
0,01
0,1
1
10
100

FIGURE 2

REFERENCES CITED IN THE DESCRIPTION

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Extrudált SCR szűrő

Szabadalmi igénypontok

1. Nitrogénoxidoknak redukálószer jelenlétében történő átalakítására szolgáló katalizátort tartalmazó faláramú szűrő, mely faláramú szűrő egy extrudált szilárd testet tartalmaz, mely:
10-95 tömeg% legalább egy kötőanyag/mátrix komponenst;
5-90 tömeg% zeolitos molekulaszitát, nem-zeolitos molekulaszitát vagy ezek közül bármely kettő vagy több keverékét; és
0-80 tömeg% adott esetben stabilizált cériumoxidot tartalmaz,
ahol a katalizátor legalább egy fémet tartalmaz, ahol:
(i) a legalább egy fém a teljes extrudált szilárd testben jelen van, és ugyancsak jelen van magasabb koncentrációban az extrudált szilárd test felületénél;
(ii) a legalább egy fém a teljes extrudált szilárd testben jelen van, és ugyancsak jelen van az extrudált szilárd test felületén jelenlévő egy vagy több bevonati rétegben; vagy
(iii) a legalább egy fém a teljes extrudált szilárd testben jelen van, ugyancsak jelen van magasabb koncentrációban az extrudált szilárd test felületénél és ugyancsak jelen van az extrudált szilárd test felületén jelenlévő egy vagy több bevonati rétegben.

2. Az 1. igénypont szerinti faláramú szűrő, ahol the extrudált szilárd test tartalmaz:
10-95 tömeg% kordierítet, nitrideket, karbidokat, boridokat, intermetallikus fázisokat, lítium-alumínium-szilikátot, egy adott esetben adalékolt alumínium-oxidot, sziliciumdioxid forrást, titándioxidot, cirkóniumdioxidot, titándioxid-cirkóniumdioxidot, cirkont, titán-cirkont, és ezek közül bármely kettő vagy több keverékét;
0-80 tömeg% spinellt;
5-90 tömeg% zeolitos molekulaszitát, nem-zeolitos molekulaszitát vagy ezek közül bármely kettő vagy több keverékét, melyek bármelyike adott esetben egy vagy több fémet tartalmaz;
0-80 tömeg% adott esetben stabilizált cériumoxidot; és
0-25 tömeg% szervetlen szálat.

3. Az 1. vagy 2. igénypont szerinti faláramú szűrő, ahol a faláramú szűrő porozitása 30-80%.

4. Az előző igénypontok bármelyike szerinti faláramú szűrő, mely egy zeolitos molekulaszitát vagy egy nem-zeolitos molekulaszitát, ahol a zeolitos molekulaszita vagy a nem-zeolitos molekulaszita szerkezeti kódja a Structure Commission of the International Zeolite Association meghatározása szerint ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOF, BOG, BPH, BRE, BSV, CAN, CAS, CDO, CFI, CGF, CGS, CHA, -CHI, -CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EON, EPI, ERI, ESV, ETR, EUO, EZT, FAR, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, IHW, IMF, ISV, ITE, ITH, ITR, ITW, IWR, IWS, IWV, IWW, JBW, JRY, KFI, LAU, LEV, LIO, -LIT, LOS, LOV, LTA, LTF, LTL, LTN, MAR, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MOZ, MRE, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NES, NON, NPO, NSI, OBW, OFF, OSI, OSO, OWE, -PAR, PAU, PHI, PON, RHO, -RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBN, SBS, SBT, SFE, SFF, SFG, SFH, SFN, SFO, SFS, SGT, SIV, SOD, SOF, SOS, SSF, SSY, STF, STI, STO, STT, STW, -SVR, SZR, TER, THO, TOL, TON, TSC, TUN, UEI, UFI, UOS, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, -WEN, YUG, ZON és ezek közül bármely kettő vagy több keverékét tartalmazza.

5. A 4. igénypont szerinti faláramú szűrő, ahol a zeolitos molekulaszita vagy a nem-zeolitos molekulaszita a Structure Commission of the International Zeolite Association szerinti legfeljebb 8 gyűrűtagú pórusnyílással rendelkezik.

6. Az előző igénypontok bármelyike szerinti faláramú szűrő, ahol az (I), (ii) és (iii) jellemzők szerinti, (a) az extrudált szilárd test egészében; (b) magasabb koncentrációban az extrudált szilárd test felületénél; és (c) az extrudált szilárd test felületén elhelyezkedő egy vagy több bevonati rétegben jelenlévő legalább egy fém eltérő a más helyzet(ek)ben jelenlévő legalább egy fémtől.

7. Az előző igénypontok bármelyike szerinti faláramú szűrő, mely egy zeolitos molekulaszitát, nem-zeolitos molekulaszitát vagy ezek közül bármely kettő vagy több keverékét tartalmaz, ahol a keverékben a legalább egy fém a zeolitos molekulaszita komponenssel, a nem-zeolitos molekulaszita komponenssel vagy a zeolitos molekulaszita komponens és a nem-zeolitos molekulaszita komponensek közül egyikkel vagy mindkettővel kapcsolódik.

8. A 7. igénypont szerinti faláramú szűrő, ahol a keverékben jelenlévő, a zeolitos molekulaszitával, nem-zeolitos molekulaszitával vagy mindkét molekulaszitával kapcsolódó

fém vagy legalább egy fém mindegyike egy vagy több, átmenti fém, lantanida vagy azok közül bármely kettő vagy több keveréke közül választott fémet tartalmaz.

9. A 8. igénypont szerinti faláramú szűrő, ahol az átmeneti fém egy IB csoportba tartozó fém, egy IVB csoportba tartozó fém, egy VB csoportba tartozó fém, egy VIIB csoportba tartozó fém és egy VIIIB csoportba tartozó fém közül választott.

10. A 8. vagy 9. igénypont szerinti faláramú szűrő, ahol az átmeneti fém Fe, Cu, Ce, Hf, La, Mn, Pt, Au, Ag, In, Rh, V, Ir, Ru, és Os közül választott.

11. Az előző igénypontok bármelyike szerinti faláramú szűrő, mely szűrő lényegében
10-95 tömeg% kordieritet, nitrideket, karbidokat, boridokat, intermetallikus fázisokat, lítium-alumínium-szilikátot, egy spinellt, egy adott esetben adalékolt alumínium-oxidot, titándioxidot, cirkóniumdioxidot, titándioxid-cirkóniumdioxidot, cirkont, és ezek közül bármely kettő vagy több keverékét;
0-30 tömeg% szilíciumdioxid forrást;
50-90 tömeg%, 1-20 tömeg%, Cu, Fe és Ce közül választott egy vagy több fémet tartalmazó nem-zeolitos molekulaszitát; és
0-20 tömeg% szervetlen szálakból álló extrudált szilárd testet tartalmaz.

12. Az előző igénypontok bármelyike szerinti faláramú szűrő, ahol a legalább egy kötőanyag/mátrix komponens kordierit, nitridek, karbidok, boridok, intermetallikus fázisok, lítium-alumínium-szilikát, egy spinell, egy adott esetben adalékolt alumínium-oxid, egy szilíciumdioxid forrás, titándioxid, cirkóniumdioxid, titándioxid-cirkóniumdioxid, cirkon, és ezek közül bármely kettő vagy több keveréke közül választott.

13. Eljárás az előző igénypontok bármelyike szerinti faláramú szűrő előállítására, melynek során:
legalább egy mátrix komponens vagy egy vagy több prekurzorja; zeolitos molekulaszita, nem-zeolitos molekulaszita vagy zeolitos és nem-zeolitos molekulaszináták keveréke, mely zeolitos molekulaszita, nem-zeolitos molekulaszita vagy a zeolitos és nem-zeolitos molekulaszináták keveréke adott esetben legalább egy fémmel kapcsolódik; adott esetben egy adott esetben stabilizált cériumoxid; és legalább egy fémvegyület poralakú kiindulási anyagok összekeverésével, adott esetben szervetlen szálakkal; és adott esetben egy szerves segédanyag hozzáadásával szilárd extrudált testet alakítunk ki;
adott esetben legalább egy fém fémsóját tartalmazó savas vagy bázikus vizes oldatban keveréssel és/vagy eldörzsöléssel képlékeny összetétellé feldolgozva keveréket hozunk létre;

a keveréket katalizátor testté extrudáljuk, a katalizátor testet szárítjuk és kalcináljuk egy szilárd extrudált test előállítására;
a kiindulási anyagok mennyiségét úgy választjuk meg, hogy a szilárd extrudált test 10-95 tömeg% legalább egy mátrix komponenst, 5-90 tömeg% zeolitos molekulaszitát, nem-zeolitos molekulaszitát vagy ezek közül bármely kettő vagy több keverékét; és 0-80 tömeg% adott esetben stabilizált cériumoxidot, és legalább egy fémet vagy fémvegyületet tartalmazzon, és a szilárd extrudált test felületét legalább egy fémmel impregnáljuk, és/vagy a szilárd extrudált test felületét legalább egy, legalább egy fémet tartalmazó réteggel vonjuk be.

14. Eljárás rögzített helyzetű vagy járművekben levő belső égésű motorok kipufogógáz kibocsájtásának kezelésére, melynek során a nitrogéntartalmú redukálószerrel kevert kipufogógázt az 1-12. igénypontok bármelyike szerinti faláramú szűrővel érintkeztetjük.

15. Kipufogórendszer belső égésű motorhoz, mely kipufogó rendszer egy 1-12. igénypontok bármelyike szerinti faláramú szűrőt, egy nitrogéntartalmú redukálószert, és a nitrogéntartalmú redukálószert a kipufogógáz áramba a faláramú szűrőhöz képest áramlásirányban felfelé betápláló eszközt tartalmaz.

16. Jármű, mely egy belsőégésű motort és egy 15. igénypont szerinti kipufogó rendszert tartalmaz.

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