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(54) Title: PROCESS FOR PREPARATION OF SUPPORTS**(57) Abstract**

Process for the preparation of a ceramic foam supporting one or more inorganic oxide(s) comprising impregnation of the foam with an impregnating phase comprising the inorganic oxide(s) precursor in an impregnating medium and drying wherein the impregnating phase has a viscosity greater than 1 cps at 20 °C, preferably of from 5 to 80 cps, more preferably of from 7 to 50 cps and wherein drying is performed without substantial prior draining of impregnating phase from the ceramic foam, and use of the ceramic foams of the invention as catalytic support in a catalytic conversion process.

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PROCESS FOR PREPARATION OF SUPPORTS

The present invention relates to a process for the preparation of ceramic foams supporting inorganic oxide(s) and catalytic applications thereof, particularly the preparation of ceramic foams supporting high loadings of inorganic oxides, and applications thereof in gas treating, adsorption, as catalyst support in catalytic conversion reactions, particularly in the preparation of carbon monoxide and hydrogen by the partial oxidation of a hydrocarbon feed, in nitric oxides reduction processes, in ethylene oxidation, and the like.

Ceramic foams are known for various applications, in particular more recently as supports for catalytically active materials fulfilling several requirements simultaneously, as described in "Preparation and properties of ceramic foam catalyst supports" by MV Twigg and JT Richardson published in the "Scientific Bases for the preparation of heterogeneous catalysts" 6th International Symposium September 5-8 1994 Louvain-la Neuve, Belgium. Open pore ceramic foams and the more traditional extrudates may be made from materials with high temperature resistance, and promote surface-catalyzed reaction by means of tortuous flow patterns, in foams by virtue of connecting adjacent pores or "cells" providing non-linear channels, and in extrudate beds by virtue of random particle packing. Ceramic foams enable the passage of gases at high space velocities and acceptable pressure drop, are readily shaped and provide good conductivity but they do not offer the high surface areas available with conventional catalyst forms such as extrudates. Commercially available foams may have a BET surface area (as defined in "Adsorption surface area and

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porosity" SJ Gregg & KSW Sing, Academic Press London 1982) of typically less than 1 m²/g, in particular of about 0.2 or 0.3 m²/g after high temperature calcination for a prolonged period, which is too low to be useful in the majority of catalytic applications. A high surface area is generally accepted to be advantageous in providing a high contact area for catalytic, treating, adsorption and other surface located activities. Twigg and Richardson report an alumina washcoating technique for the stabilisation of a 30 pore per inch alpha-alumina/mullite ceramic foam at high temperature, whereby a four-fold reduction in surface area decay of the ceramic foam was achieved after calcining at 1000°C for 4 hours.

EP 0 260 826 discloses ceramic foam supports suited for use in steam reforming of methane, comprising a network of irregular passages extending therethrough, comprising supported catalytically active material and an inorganic oxide stabiliser to prevent sintering of the active material. The stabiliser and the active material are introduced by impregnation of the foam by means of immersion of the foam in an aqueous solution of a salt of the stabiliser and the active component, draining to remove excess solution and firing at 450°C. This process is repeated to build up sufficient impregnant layer on the foam. However the foams described are to be used at relatively low temperatures, of the order of 760°C, and may not give the desired stabilisation at higher temperatures. This process is suited for the stabilisation of the active component in the existing (low) surface area foam, but does not address enhancing the surface area of the existing low surface area foam. The application of this process for enhanced surface area of the low surface area foam would be laborious and time consuming.

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FR 2 590 887 discloses zirconium oxides having stable surface area at elevated temperatures, the oxide comprising as additive an oxide of silica, the rare earths, yttria, ceria and/or aluminium. The additive may be introduced by various means including co-precipitation, mixing of salt with sol hydrate and impregnation of the zirconium oxide with a salt precursor of the additive. Impregnation is preferably performed "dry" whereby the total volume of the impregnating solution is approximately equal to the total pore volume of the (oxide) support. It is taught by means of example to impregnate extruded support granules with the aqueous impregnating solution, to dry at 160°C for 16 hours and calcine at 400°C. The additive is nevertheless present in low amounts of 1 to 10wt% based on the weight of the total composition. The support may be in the form of granules or pellets. The BET surface area is increased from 20 m²/g without additive to 40-50 m²/g with additive at 900°C. This document discloses the impregnation of mesoporous structures, wherein the additive is adsorbed and crystallised onto the support. There is no reference to supports in the form of foam structures, which comprise pores of several orders of magnitude greater than the mesoporous, and for which a different mechanism of supporting of the additive is involved.

The provision of ceramic foams having significant loadings of inorganic oxides and significant increase in BET surface area remains a problem, even more so in applications employing extreme conditions typical of some processes, for which improved surface area retention is needed compared with known foam supports.

It has now surprisingly been found that the limitation on inorganic oxide loading and on surface area lies not with the concept of providing an additional layer, as is known from the referred publications, but in

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the manner of its provision, whereby full advantage is not obtained.

It has now surprisingly been found that in a particular process for the preparation of ceramic foams supporting inorganic oxide(s) a significant increase in
5 inorganic oxide loading and in surface area can be attained, which increase is still favourable at temperatures at or above 800°C.

Accordingly there is provided according to the present invention a process for the preparation of a
10 ceramic foam supporting one or more inorganic oxide(s) comprising impregnation of the foam with an impregnating phase comprising the inorganic oxide(s) in an impregnating medium and drying wherein the impregnating
15 phase has a viscosity greater than 1 cps, i.e. greater than water, and drying is performed without substantial prior draining of impregnating phase from the ceramic foam.

It is a particular feature of the invention that the use of an impregnating solution more viscous than water
20 allows significant retention of the impregnating medium in the foam pores prior to and during drying. This is a problem not encountered in the impregnation of other materials having pore sizes orders of magnitude less than
25 typically found in ceramic foams. It has been found that the resulting impregnated material has superior characteristics, particularly in terms of solid loading and retention of enhanced surface area on high temperature calcining, to materials impregnated by known
30 methods of aqueous "wet" impregnation or wash coating.

Suitably the impregnating phase has a viscosity of greater than 1 cps at 20°C, preferably of from 5 to 80 cps, more preferably from 7 to 50cps. A suitable
35 viscosity may be selected according to the properties of the ceramic foam, in particular the pore size thereof,

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whereby a smaller pore size would require a less viscous impregnating phase.

Suitably the drying is performed without substantial prior draining of impregnating medium from the ceramic foam. Reference herein to "substantial prior draining" is to draining practices common in the art of washcoating and impregnation, and which may involve subjecting the foam to vacuum, centrifuging or blowing air through the foam for example. It is intended that substantially none of the impregnating medium introduced into the foam pores should be deliberately removed but rather should be allowed to be retained, aided by the viscosity thereof.

Suitably therefore, any drainage of impregnating medium from the foam pores prior to drying is less than 60%, preferably less than 50%, more preferably from 0% to 40% of that introduced. Preferably the pores of the foam are substantially filled with impregnating medium prior to drying. Preferably the foam pores are filled by at least 60% with impregnating medium, more preferably by at least 85%. Suitably the ceramic foam is immersed slowly or incrementally into the impregnating phase whereby formation of air pockets is prevented, this enabling filling of the pores. The rate of immersion or extent of initial immersion may be determined appropriately according to the pore size (ppi) of the foam, and the viscosity of the impregnating medium. The impregnation may be carried out at or below atmospheric pressure. With use of foams of low pore diameters it may be particularly advantageous to impregnate at reduced pressure of between 0.5 and 1 atmospheres. The pore volume may be calculated for example on the basis of the density, weight and dimensions of the foam, whereby the amount of impregnating medium required may be determined.

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Drying may be performed by any known means, such as subjecting to air-flow at ambient temperature, oven drying or microwave drying.

5 Any undesired displacement of impregnating medium during drying may conveniently be avoided by rotation of the foam, other suitable means.

10 There is, however, provided in a further aspect of the invention the option to deliberately induce the displacement of the impregnating phase and thereby allow a gradient of impregnant to develop. This has the advantage of providing a gradient in solids loading and surface area which may not be obtained by synthetic means. This may be achieved for example by selection of a slightly less viscous impregnating phase than would
15 otherwise be appropriate for a given foam sample. Reference herein to a "gradient" in any given property of the foam samples of the invention is to a stepwise or continuous change in value of that property, such as surface area, solids loading for example, across a given
20 dimension of the impregnated foam sample.

The impregnating medium may be in the form of any suitable liquid having viscosity greater than that of water. Suitably the impregnating medium is in the form of an aqueous or organic solution, slurry, sol, gel,
25 suspension or dispersion of inorganic oxide(s) particles, preferably of a sol of colloidal inorganic oxide(s) particles. The preparation of such impregnating media is well known in the art. A sol may be prepared in particular by means of peptising a slurry of the
30 inorganic oxide(s) or precursor thereof. Alternatively where it is desired to impregnate a ceramic foam with more than one inorganic oxide, a commercially available sol, for example an alumina sol may be adapted by the addition of the further inorganic oxide(s).

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The impregnating phase may be stabilised to attain an inorganic oxide(s) particle size of less than 300 nm, preferably less than 150 nm, more preferably in the range of 5 to 50 nm. Stabilisation may be performed by any known means, for example by electrostatic stabilisation or "depletion" stabilisation by addition of a polymer or other impregnating medium modifier. It may be additionally advantageous to treat the impregnating phase to minimise the content of inorganic particles greater than 300 nm, preferably greater than 150 nm, more preferably greater than 50 nm, for example by means of ultrasound. This is of particular advantage with use of ceramic foams of small pore dimensions.

Suitably the impregnating phase employed has a solid content of greater than 5 wt% whereby a sufficient amount of inorganic oxide(s) precursor is introduced into the pores. Preferably the solids content is between 7 and 40 wt%, the maximum solids loading depending on the loading at which inorganic oxide(s) precursors particles dispersion deteriorates, or flocculation occurs. At significantly lower solids loadings, the formation of a coherent film will be inhibited.

Preferably the foam is pretreated prior to impregnation, in order to improve the dispersion and cohesion of the eventual impregnated oxides. A pretreatment of the foam with water and drying to give an optimised concentration of surface hydroxide groups, for example, prior to impregnation with the inorganic oxide(s) has been found to give improved impregnation of the foams.

The dried impregnated inorganic oxide may be in the form of a coherent or incoherent film coating of the ceramic foam as will be understood with reference to thin film coating technology. A calcined ceramic foam having a coherent film coating will generally exhibit attractive

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surface area enhancement having high stability and is particularly preferred where it is desired to modify the bulk properties of the ceramic foam. This has found to be attained with the use of impregnating medium in the form of a coherent dispersion, preferably a dispersion of colloidal particles in liquid. A coherent film coating may for example be derived from a partially dried impregnated oxide in the form of a hydrogel, in particular from impregnation of an impregnating phase characterised by a gelling time substantially equal to its drying time or, where gelling commences during impregnation, to the combined impregnation and drying time.

Suitably the ceramic foams of the invention comprise a layer of the inorganic oxide of thickness greater than 0.5 micron, preferably of greater than 1 micron. The ceramic foams of the invention typically are obtained with a layer of the inorganic oxide of up to 2.5 micron. The thickness of the layer may be determined by choice of inorganic oxide(s) solid content of the impregnating phase. In general, the greater the layer thickness the greater the increase in surface area of the foam, and the greater the tortuosity and pressure drop presented by the foam.

Suitable ceramic foams to be employed in the present invention are for example those having from 10 pores per inch. Commercially available foams are generally in the range of up to 200 pores per inch. The choice of foam will generally depend on the intended use, whereby selection of material from high temperature stable single or mixed refractory oxides of silica, alumina, titania, zirconia and (partially) stabilized forms thereof, carbides, nitrides and mixtures thereof may confer beneficial properties such as thermal stability, thermal shock resistance and/or strength, and whereby increase in

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pores per inch rating generally corresponds to an increase in tortuosity of a fluid passed through the foam. In specific applications for example where pore surface contact of a fluid passing at high space velocities through the foam is desired, there is a need for a high tortuosity foam. The term "tortuosity" is a common term which, when referring to a fixed catalyst bed, can be defined as the ratio of the length of the path taken by a gas flowing through the bed to the length of the shortest straight line path through the bed. Thus a non-tortuous bed, such as a honeycomb monolith structure, has a tortuosity of 1.0. Suitably ceramic foams of the present invention have a tortuosity of at least 1.1, for example of 1.1 to 10.0, more preferably of 1.1 to 5.0, most preferably of 1.3 to 4.0.

It is a particular advantage of the present invention that the process is substantially independent of the size, shape or other dimension of foam sample being impregnated. Suitably foams of any dimensions or scale may be impregnated and yield excellent results, for example foams of the order of centimetres to order of metres, preferably of dimension in any given direction of 0.5 cm to 1 m.

The inorganic oxide(s) to be impregnated according to the process of the invention may suitably comprise any ambient or high temperature stable high surface area inorganic oxide. Such oxides may include but are not limited to oxides comprising one or more cations selected from groups IA, IIA, IIIA and IVA of the Periodic Table of the Elements and the transition metals (Periodic Table of the Elements, IUPAC 1970), preferably from groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VB, VIB, VIIB, VIII and the lanthanides, more preferably from aluminium, lanthanum, titanium, magnesium, yttrium, silicon, zirconium, cerium, niobium and barium. Preferred

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inorganic oxides to be impregnated in ceramic foams employed as catalytic supports in a process for the preparation of carbon monoxide and hydrogen by the partial oxidation of a hydrocarbon feedstock include those above defined, more preferably oxides comprising aluminium as the only cation or comprising more than one of the above defined cations. The foam may be impregnated with more than one inorganic oxide (precursor) simultaneously or sequentially.

Inorganic oxides comprising more than one of the above cations present several advantages, for example an oxide may be employed comprising one cation as above defined, such as lanthanum giving desired performance in the intended use of the foam, together with a further cation as above defined, such as aluminium of which the precursor is readily dispersed in the impregnating phase. By this means the solids loading may be increased without prejudicing the performance of the impregnated material. In a preferred embodiment the present invention relates to the impregnation of ceramic foams as hereinbefore defined with an impregnating phase having enhanced solids content of inorganic oxide precursor comprising a first cation as hereinbefore defined, by inclusion or increased content of a second cation as hereinbefore defined of which the inorganic oxide precursor is characterised by a higher dispersion capacity in the impregnating phase, preferably a second cation is aluminium.

Ceramic foams prepared according to the present invention may suitably comprise a catalytically active component as the inorganic oxide or in addition to the inorganic oxide. A catalytically active component may thus be impregnated as the inorganic oxide onto the ceramic foam or may be impregnated onto the inorganic oxide supported ceramic foam. Many catalytic applications are envisaged, of which particular advantage may be

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by employing as preferred catalytically active components to be impregnated in ceramic foams employed as catalytic supports those generally known for a process for the preparation of carbon monoxide and hydrogen by the partial oxidation of a hydrocarbon feedstock, including a metal or precursor of a metal selected from Group VIII of the Periodic Table of the Elements, preferably selected from ruthenium, rhodium, palladium, osmium, iridium and platinum, more preferably rhodium, platinum and iridium, for a process for nitric oxides reduction, including vanadium, titanium and a mixture thereof, and for a process for the manufacture of ethylene oxide.

In a further aspect the present invention provides the use of ceramic foams obtained as above defined as a catalytic support in a catalytic conversion process. Particular advantages are obtained with the use of ceramic foams obtained as above defined as a catalytic support in a conversion process employing temperatures greater than or equal to 800°C, preferably employing space velocities greater than or equal to 500,000 Nl/kg/hr, more preferably in a process for preparation of carbon monoxide and hydrogen by the partial oxidation of a hydrocarbon feed.

Ceramic foams according to the invention may also be employed in gas treating applications. Many applications are envisaged, of which particular advantage may be obtained in guard bed application for removing impurities or undesired components of a gas stream, particularly for purification or feed conditioning purpose, or in other gas adsorption or filtration application, particularly for separating components of a mixed gas stream, optionally with suitable active components loaded onto the modified foam.

As hereinbefore mentioned, it may be desired to perform the process of the invention in such a manner

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that impregnating medium is displaced during the drying stage, to form a gradient of impregnant.

Particular applications of such gradient may be foreseen in applications involving catalytic reaction, wherein distribution of catalytically active material may be manipulated by means of adoption of gradient created by the impregnant, or in applications involving feed conditioning, adsorption etc., in which different velocities and retention times may be desired for components of a mixed gas stream passing through the foam.

Accordingly in a further aspect of the invention there is provided a process for the catalytic partial oxidation of a hydrocarbon feedstock, which process comprises contacting a feed comprising the hydrocarbon feedstock, and an oxygen containing gas at an oxygen-to-carbon molar ratio in the range of from 0.45 to 0.75 at elevated pressure with a catalyst in a reaction zone, which catalyst comprises a metal selected from Group VIII of the periodic table supported on a ceramic foam carrier, wherein the metal is present in the form of a gradient as hereinbefore defined.

The invention is now illustrated by means of non-limiting examples.

Example 1 - Preparation of a composition of the invention

Rectangular samples (approximately 4 x 4 x 1 cm) of alpha alumina foams with 30 pores per inch were modified by sol impregnation with boehmite sol, (Nyacol Al₂O₃) having a solid content of 20 wt% on Al₂O₃ basis and a viscosity of 10 cps. Before impregnation with the sol the foams were first impregnated with water and dried at 55 to 60°C. Impregnation with the sol was then effected by immersing it, first partly and after 2 hours fully in the sol for 6 hours under 0.8 atmosphere vacuum. The samples were transferred to a drying oven with substantially no

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loss of impregnating medium from the pores and were then dried at 55 to 60°C for 12 to 14 hours. After drying the samples were calcined at temperatures ranging from 800 to 1100°C for 8 hours. The foams were weighed before
5 modification and after drying and calcination. Samples of the unimpregnated alpha alumina foams with 30 pores per inch were also weighed, calcined at temperatures ranging from 800 to 1100°C for 8 hours and reweighed for comparison purpose.

10 Example 2 - Preparation of a composition of the invention

Rectangular samples (approximately 4 x 4 x 1 cm) of partially stabilised zirconia (Zr - Mg + Ca) foams with 50 pores per inch were modified by sol impregnation with
15 lanthana alumina sols having a solids content of 13wt% on oxide basis and a viscosity of 10 cps according to the process of Example 1. The sols were obtained by adding lanthanum nitrate solution to a commercial alumina sol (Nyacol Al₂O₃). The samples were then dried at 55 to 60°C for 12 to 14 hours. After drying the samples were
20 calcined at temperatures ranging from 1100 to 1300°C for 8 hours. After the first impregnation some samples were calcined at 600°C and then subjected to a second impregnation treatment. A sample of the impregnation sol was weighed, dried and calcined to a gel under the same
25 conditions as the foams and reweighed. The foams were weighed before modification and after drying and calcination.

Example 3 - Preparation of a composition of the invention

30 Rectangular samples (approximately 4 x 4 x 1 cm) of partially stabilized zirconia (Zr - Mg + Ca) foams with 50 pores per inch were modified by the same technique of examples 1 and 2, using titania sols prepared by the hydrolysis of titanium isopropoxide, of 0.3 mole/l. The modified foams were dried and then heated at 450 °C for

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8 hours. Some samples were subjected to a second impregnation step thereafter.

Surface area measurements were made by known techniques for recording BET surface area.

5 The results for Examples 1, 2 and 3 are given in Tables 1 and 2 below, Table 1 giving % weight gain, and (by FE-SEM pictures) layer thickness.

10 TABLE 1 - Weight gain, and impregnated layer thickness for compositions of examples 1 after calcination at different temperatures for 8 hours.

Sample of Expt no./calcination T (°C)	Initial weight of foam (g)	% weight gain relative to initial weight	Thickness of impregnated layer micron)
1 / 800	8.01	44	2.5
1 / 900	8.09	44	2.3
1 / 1000	8.25	41	2.0
1 / 1100	8.65	40	1.2

TABLE 2 - Measured BET surface area (SA) for untreated foams and compositions of Examples 1 and 2 after calcination at different temperatures for 8 hours.

Sample of Expt No./pores per inch	Calcination Temperature and time (°C, hours)	SA of untreated foam (m ² /g)	SA dried/- calcined impregnating sol (m ² /g)	SA of calcined impregnated foam (m ² /g)	SA of calcined washcoat foam (m ² /g)
1 / 30	800 / 8	<0.1 calcined	108	66	
1 / 30	900 / 8	<0.1 calcined	94	41	
1 / 30	1000 / 8	<0.1 calcined	15	4.9	
1 / 30	1100 / 8	<0.1 calcined	4.1	1.8	
Comp. 1 / 30	1000 / 4	1.0 fresh			4.0
2 / 50	1000 / 8	0.23 calcined	78	4.0	
2 / 50	1100 / 8	0.23 calcined	55	3.6	
2 / 50	600 / 8 1100 / 8	0.23 calcined		7.0 (2x impregnated)	
2 / 50	600 / 8 1300 / 8		9.6	0.9 (2x impregnated)	
3 / 50	450 / 8			6.0 (2x impregnated)	
6 / 20	1100 / 8	0.5		1.2	

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1 Alumina washcoat stabilisation of a 30 pore per inch
alpha-alumina/mullite ceramic foam calcined at 1000°C
for only 4 hours, as reported in "Preparation and
properties of ceramic foam catalyst supports" by MV
5 Twigg and JT Richardson published in the "Scientific
Bases for the preparation of heterogeneous catalysts"
6th International Symposium September 5-8 1994 Louvain-
la-Neuve, Belgium.

After calcining at 900°C and 1000°C for 8 hours the
10 compositions of Example 1 according to the invention
give surface areas of the order of 400 and 50 times the
starting surface area of the unmodified foam. This is
favorably comparable with the comparison¹ calcined
under less severe conditions.

15 The compositions of Example 2 calcined at 1000°C
and 1100°C give favourable stabilisation of surface
areas of a partially stabilised zirconia foam, when
compared with measured surface areas of the
corresponding dried and calcined impregnating sol.
20 Exceptionally high surface areas may be obtained with
repeated impregnation as illustrated in Example 2.

Example 4 - Preparation of a catalyst of the invention

The modified foam samples according to Example 2
but of dimension 11 mm x 4 mm were loaded with
25 catalytically active metal rhodium, by means of
impregnation with an aqueous solution of rhodium
chloride, having a metal concentration of 10 to 20%. By
weighing before and after, a suitable loading could be
determined, which was 5 wt% of rhodium metal.

30 Example 5 - Conversion process using catalyst of the
invention

The foams samples modified according to Example 2
(calcined at 1100 °C) and 4, were loaded into an
autothermal microflow reactor for the partial oxidation
35 of methane, consisting of an elongate quartz tube,

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maintained at 3 bar during operation. Hydrocarbon (methane) and oxygen at room temperature were mixed in O₂/C ratio of 0.5-0.65 mol/mol and led, at a velocity of around 500,000 Nl/l/h, through the reactor operated autothermally at 950-1100 °C. The gaseous effluent was analysed on exiting the reactor, and results are given in Table 3.

For comparison purposes the conversion was repeated using a similar sized unmodified foam as used as starting foam in Example 2, loaded with rhodium metal as described in Example 4.

TABLE 3

Example	Surface Area m ² /g	Temperature °C	CH ₄ Conversion C%	H ₂ selectivity %
5	3.6	1020 (904)	93.2	91.0
5 (comparison)	0.1	1200 (904)	85.1	86.1

As is apparent from the table, a surprising result was found when comparing the performance of the catalyst of the invention with a standard (unmodified foam) catalyst, in terms of the temperature recorded at the front of the foams. The beneficial lower temperature observed according to the invention is indicative of a superior performance of the catalytic metal, as is seen in the conversion and selectivity obtained.

This result was not to be expected, and represents a significant advantage of application of the foams of the invention.

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Similar performances were observed with catalysts comprising 30 pore per inch alumina foam and 80 pore per inch partially stabilized zirconia (Zr-Mg) modified according to Example 2, in the process of Example 5 wherein temperatures at the front of the modified foam catalysts were recorded 200 °C lower than observed with unmodified foams.

Example 6

A sample (of 30 x 4 x 1 cm) of zirconia stabilized alumina (ZTA) foam with 20 pores per inch was modified according to the procedure of Example 1, employing vacuum during the 2 to 3 hours immersion in the impregnation medium. During transfer to the drying stage drainage of impregnating medium from the pores was about 37 %wt.

The dried foam was calcined for 8 hours at 1100 °C. XPS revealed a gradient of alumina had developed in the foam, such that the Al/Zr atomic ratio varied between 38 and 65, compared with a ratio of 5 in the starting material. The foam was loaded with rhodium following the technique of Example 4.

Example 7 - Conversion process using catalyst of the invention

The modified and rhodium-loaded foam catalyst of Example 6 was employed in a larger scale version of the conversion process of Example 5, in which feed was preheated and catalyst was pre-ignited using methanol and air. The results are given in Table 4.

For comparison purposes, the conversion was repeated using a sample of the corresponding unmodified foam loaded with rhodium metal as in Example 4.

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TABLE 4

Example	Conversion %	CO-selectivity %	H ₂ selectivity %
7	81.8	93.4	86.7
7 (comparison)	80.4	91.0	83.7

5 A superior performance is apparent, which indicates that the invention is highly robust to variations in size of modified foam employed, and moreover in uniformity of impregnation, such that indeed gradient impregnation can be tolerated.

10 Further applications of the modified foams which may positively benefit from gradient impregnation are also included within the scope of this invention, in particular employing a selected orientation of the gradient in the Example 7, for example with maximum Al/Zr atomic ratio at the catalyst front, whereby further enhanced temperature control and selectivity may be envisaged.

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C L A I M S

1. Process for the preparation of a ceramic foam supporting one or more inorganic oxide(s) comprising impregnation of the foam with an impregnating phase comprising the inorganic oxide(s) precursor in an
5 impregnating medium and drying wherein the impregnating phase has a viscosity greater than 1 cps at 20°C, and wherein drying is performed without substantial prior draining of impregnating phase from the ceramic foam.
2. Process according to claim 1 wherein the
10 impregnating phase has a viscosity of from 5 to 80 cps at 20°C, preferably of from 7 to 50 cps.
3. Process according to any of the preceding claims wherein any drainage of impregnating medium from the pores prior to drying is less than 60%, preferably less
15 than 50%, more preferably from 0% to 40% of that introduced.
4. Process according to any of the preceding claims wherein pores of the ceramic foam are substantially filled with impregnating medium prior to drying,
20 preferably are filled by at least 60%, more preferably by at least 85% prior to drying.
5. Process according to any of the preceding claims wherein a gradient of impregnant is developed by deliberately induced displacement thereof.
- 25 6. Process according to any of the preceding claims wherein the impregnating phase is in the form of an aqueous or organic solution, slurry, sol, gel, suspension or dispersion of inorganic oxide(s) precursor particles, preferably of a sol of colloidal
30 inorganic oxide precursor particles.

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7. Process according to any of the preceding claims wherein the impregnating phase is stabilised to attain an inorganic oxide(s) particle size of less than 300 nm, preferably less than 150 nm, more preferably in the range of 5 to 50 nm, preferably is electro-statically stabilised or stabilised by addition of a polymer or other impregnating medium modifier.

8. Process according to any of the preceding claims wherein the impregnating phase is treated to minimise the content of inorganic oxide precursor particles greater than 300 nm, preferably greater than 150 nm, more preferably greater than 50 nm, for example by means of ultrasound.

9. Process according any of the preceding claims wherein the dried impregnated inorganic oxide precursor is in the form of a coherent or incoherent film coating of the ceramic foam.

10. Process according to any of the preceding claims wherein the partially dried impregnated oxide precursor is in the form of a hydrogel.

11. Process according to any of the preceding claims wherein the impregnating phase is characterised by a gelling time substantially equal to its drying time or to the combined impregnating and drying time.

12. Process according to any of the preceding claims wherein the impregnating phase has a solid content of greater than 5 wt%, preferably of between 7 and 40 wt%,

13. Process according to any of the preceding claims wherein the ceramic foam is comprised of a high temperature stable refractory oxide for example selected from oxides of silica, alumina, titania, zirconia and (partially) stabilized forms thereof, carbides, nitrides and mixtures thereof.

14. Process according to any of the preceding claims wherein the ceramic foam has a tortuosity as herein

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defined in the range of from 1.1 to 10.0, preferably 1.1 to 5.0, more preferably from 1.3 to 4.0.

15. Process according to any of the preceding claims wherein the inorganic oxide(s) comprise one or more
5 cations selected from groups IA, IIA, IIIA and IVA of the Periodic Table of the Elements and the transition metals, preferably from groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VB, VIB, VIIB, VIII and the
10 lanthanides, more preferably from aluminium, lanthanum, titanium, magnesium, yttrium, silicon, zirconium, cerium, niobium and barium.

16. Process according to any of the preceding claims wherein the solids content of inorganic oxide precursor in the impregnating phase is enhanced by means of
15 including in or increasing the content in the precursor of an inorganic oxide comprising a first cation as defined in claim 15, of a second cation as defined in claim 15 of which the inorganic oxide precursor is characterised by a higher dispersion capacity in the
20 impregnating phase, preferably a second cation is aluminium.

17. Process according to any of the preceding claims wherein a catalytically active component is impregnated as the inorganic oxide onto the ceramic foam or is
25 impregnated onto the inorganic oxide supported ceramic foam.

18. Process according to claim 15 wherein the catalytically active component comprises a metal or precursor of a metal selected from Group VIII of the
30 Periodic Table of the Elements, preferably selected from ruthenium, rhodium, palladium, osmium, iridium and platinum, more preferably rhodium, platinum and iridium.

19. Use of ceramic foams prepared according to the
35 process of any of the preceding claims in gas treating,

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adsorption, as a catalytic support in a catalytic conversion process or the like.

20. Use of ceramic foams according to any of preceding claims as a catalytic support in a high pressure drop conversion process employing temperatures greater than or equal to 800°C, preferably employing space velocities greater than or equal to 500,000 Nl/kg/hr, more preferably in a process for preparation of carbon monoxide and hydrogen by the partial oxidation of a hydrocarbon feed.

21. Process for the catalytic partial oxidation of a hydrocarbon feedstock, which process comprises contacting a feed comprising the hydrocarbon feedstock, and an oxygen containing gas at an oxygen-to-carbon molar ratio in the range of from 0.45 to 0.75 at elevated pressure with a catalyst in a reaction zone, which catalyst comprises a metal selected from Group VIII of the periodic table supported on a ceramic foam carrier, wherein the metal is present in the form of a gradient as hereinbefore defined.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 95/04713

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J37/02 B01J35/04 B01J35/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE,A,34 33 197 (SAKAI CHEMICAL INDUSTRY CO) 28 March 1985 see example 1 see claim 1	1,2,15, 18,19
Y	EP,A,0 198 186 (DRACHE KERAMIKFILTER) 22 October 1986 see claims 1,7	1,2,15, 18,19
A	PATENT ABSTRACTS OF JAPAN vol. 012 no. 353 (C-530) ,21 September 1988 & JP,A,63 111944 (TOYOTA MOTOR CORP;OTHERS: 01) 17 May 1988, see abstract	
A	FR,A,2 316 906 (MONTEDISON SPA) 4 February 1977	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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