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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 February 2006 (23.02.2006)

PCT

(10) International Publication Number
WO 2006/018059 A2

(51) International Patent Classification[7]: C01B 17/78, B01J 35/04

(21) International Application Number: PCT/EP2005/006800

(22) International Filing Date: 23 June 2005 (23.06.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PA 2004 01250 19 August 2004 (19.08.2004) DK

(71) Applicant *(for all designated States except US)*: **HALDOR TOPSØE A/S** [DK/DK]; Nymøllevej 55, DK-2800 Kgs. Lyngby (DK).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **HYLDTOFT, Jens, Henrik** [DK/DK]; Østbyvej 9, DK-4050 Skibby (DK). **PEDERSEN, Henrik, Guldberg** [DK/DK]; Vennemindevej 17, 2.th., DK-2100 Copenhagen Ø (DK). **TEUNISSEN, Herman** [NL/DK]; Postmosen 56, DK-3400 Hillerød (DK).

(74) Common Representative: **HALDOR TOPSØE A/S**; Nymøllevej 55, DK-2800 Kgs. Lyngby (DK).

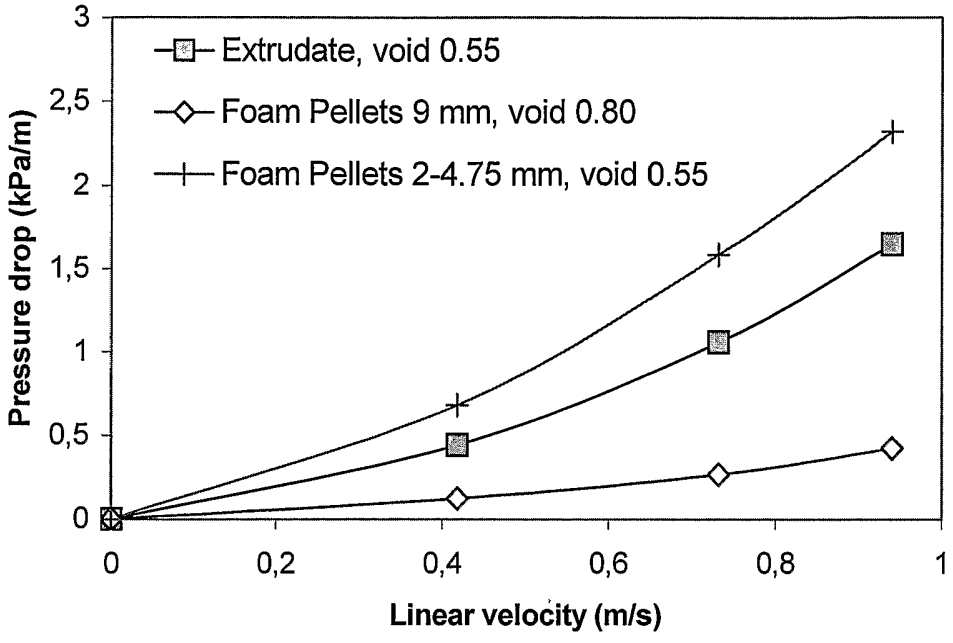
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** PROCESS AND CATALYST FOR THE OXIDATION OF SO_2 TO SO_3



(57) **Abstract:** A process for the catalytic oxidation of sulphur dioxide to sulphur trioxide comprising contacting SO2 under oxidation conditions with a monolithic catalyst comprising a reticulated ceramic foam having at its surface a wash coated layer of high surface area oxide serving as carrier for the active catalytic material platinum.

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Process and Catalyst for the Oxidation of SO_2 to SO_3

BACKGROUND OF THE INVENTION

The present invention relates to a process and catalyst for the catalytic oxidation of sulphur dioxide to sulphur trioxide. More particularly, the invention relates to reticulated ceramic foam catalysts having a high surface to volume ratio containing a catalytically active phase for use in the oxidation process.

DESCRIPTION OF RELATED ART

Commercial heterogeneous catalysts generally consist of porous inorganic solids optionally in combination with one or more metals. These catalyst systems need to be shaped in a rational way in order to fulfil the requirements regarding e.g. catalytic performance, mechanical strength and pressure drop. Fixed bed catalysts can traditionally be in the form of pellets, extrudates or monoliths as known by those skilled in the art.

In the last decade, however, foam catalysts have received considerable attention due to the combination of several attractive features (M. V. Twigg and J. Richardson, Stud. Surf. Sci. Catal. Prep. of Catalysts VI. 91 (1995) 345). Ceramic foams are characterised by a continuous, highly porous structure constituted of interconnecting cells. This megaporosity, in which the pore size typically varies from 0.04 to 1.5 mm, gives rise to a highly tortuous flow pattern in which turbulence is significantly enhanced. This leads to forced convective flow and better convective heat

transfer. Due to the megaporosity, the pressure drop is relatively low enabling a high space velocity. Finally, the reticulated cellular structure provides a high surface area to volume ratio which simulates very small pellet diameters and gives rise to low diffusion resistance. Additionally, a large surface area can be applied at the foam by wash coating it with a layer of a high surface area oxide.

In general, the optimal catalyst shape is dependant on the detailed process conditions. For a process that is not diffusion limited the catalytic activity depends on the surface area of active material. For a process which is diffusion limited the activity is increased by increasing the geometric surface area per unit volume. While decreasing the size of pieces constituting a catalyst bed has the effect of increasing the surface area per unit volume, it has the adverse effect of increasing the pressure drop resulting from the flow of reactants. Usually, it is desirable to minimise pressure drop. Furthermore, catalytic reactions generally involve the absorption or evolution of heat and the geometrical shape affects the transfer of heat to or from the reactants to a significant extent.

In relation to a fixed bed composed of pellets, ceramic foam possesses clear advantages with respect to a relatively low pressure drop and improved heat and mass transfer characteristics. Catalysts in the form of monoliths possess to a considerable extent the same advantages as ceramic foams, but they lack the highly tortuous flow pattern and the improved convective heat transfer. On the contrary, monoliths show even lower pressure drops enabling extremely high space velocities.

The pressure drop by gas flow through a fixed bed is determined by the void fraction and the equivalent particle size [R.B. Bird, W.E. Stewart and E.N. Lightfoot, Transport Phenomena, John Wiley & Sons, 1960]. The equivalent particle size (hydraulic diameter) is calculated from the geometric surface area per reactor volume. High void fraction or large equivalent particle size results in lower pressure drop than low void fraction or small equivalent particle size at given gas flow rate. For foams the equivalent particle size relates to the pore diameter and the skeleton geometry. Small pores corresponds to high surface area per unit volume and consequently to a small equivalent particle size [J.T. Richardson, Y. Peng and D. Remue, Applied Catalysis A: General volume 204 (2000), 19-32].

The relations between the equivalent particle diameter area per unit bed volume and void fraction is described by R. B. Bird, W.E. Stewart and E.N. Lightfoot in Transport Phenomena, John Wiley & Sons, 1960, and is given by:

$$a = a_v*(1-\varepsilon) \text{ and } D_p = 6/a_v, \text{ where}$$

a is the specific particle area per reactor volume (m^2/m^3)
a_v is the specific particle area per particle volume (m^2/m^3)
ε is the void fraction and
D_p is the equivalent particle diameter (m).

Typical values for area per unit volume for ceramic foams are given by Richardson et al. [J.T. Richardson, Y. Peng

and D. Remue, Applied Catalysis A: General volume 204 (2000), 19-32].

The prior art reveals many examples of catalytic processes in which the specific advantages of foam based catalysts as outlined above are demonstrated. These processes involve production of synthesis gas by catalytic partial oxidation (WO patent application 01/60515, US patent No. 5,658,497, WO 96/16737) steam reforming (US patent No. 6,409,976, EP 0260826) and autothermal reforming (WO 0076651). Other examples involve the oxidation of ammonia (US patent No. 5,336,656), selective catalytic reduction (US patent Nos. 6,040,266, US 5,422,085), oxidative dehydrogenation (US patent No. 6,072,097), CO oxidation (US patent No. 5,112,787) and catalytic combustion (US patent No. 6,077,600). However, oxidation of sulphur dioxide to sulphur trioxide, which is the basis for commercial sulphuric acid manufacturing, has apparently not been published using foam based catalysts.

The production of sulphuric acid is commercially achieved by alkali promoted vanadium based catalysts as is known to those skilled in the art. In addition, Pt based catalysts are well known and have higher activity compared to the vanadium based catalysts, though they are not applied commercially due to their much higher price. US patent No. 5,264,200 contains an extensive description of the prior art and reveals that both vanadium and Pt based catalysts have been described on particulate and monolithic substrates. In addition, US patent No. 5,264,200 discloses monolithic catalysts both with respect to vanadium and Pt based systems. In detail, the monoliths are preferably sil-

ica extruded in nominally 100 to 300 cpsi with square cells. Furthermore, a wash coat is applied involving SiO_2 and preferably ZrO_2 as a promoter compound. Finally, the Pt catalysts are obtained using conventional ion-exchange techniques. These catalysts are applied in an adiabatic process comprising four beds with SO_3 absorption after the second and fourth bed. More specifically, the first, second and third bed contain monolithic Pt based catalysts while the fourth bed contains a conventional Cs-V catalyst.

SUMMARY OF THE INVENTION

It has now surprisingly been found that the use of ceramic foam substrates, wash coated with a high surface area oxide and impregnated with platinum for oxidation of sulphur di-oxide to sulphur trioxide, utilises the platinum in a much more efficient way. This enables the use of less platinum catalyst compared to the above mentioned monoliths in the first and third beds of a reactor and also allows the use of Pt catalyst in the fourth bed of such a reactor.

It is therefore an object of the invention to provide a process for the catalytic oxidation of SO_2 to SO_3 utilising a Pt catalyst based upon reticulated ceramic foam that is wash coated with a high surface area oxide. This could for instance be TiO_2.

Reticulated ceramic foam is available in many forms from a number of commercial suppliers. The ceramic foam substrates may be in the form of a monolithic structure or as pellets. By varying the pellet size distribution it is possible to vary the void fraction in the reactor bed. By proper choice

of pore size in the foam skeleton and foam pellet size it is thus possible to adjust the bed properties to the specific requirements such as pressure drop at a given gas flow rate and amount of catalyst per unit reactor volume. Also, catalyst in the form of foam pellets is easier to load into an existing reactor than a monolithic structure.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a platinum catalyst based upon reticulated ceramic foam wash coated with a high surface area oxide for use in the catalytic oxidation of SO_2 to SO_3. Foam material is preferred as it is stable at the operating conditions and has good mechanical strength and a well-defined porosity. The foam can be made of different materials such as oxides, carbides or nitrides, preferably oxides of aluminum, titanium, zirconium or mixtures thereof. The pore density is in the range of 10 to 80 pores per inch (PPI), preferably in the range of 10 to 30 PPI. The foam substrates are sintered at high temperature to a low surface area and have a skeleton porosity in the range of 0% to 50%, preferably in the range of 10% to 40%.

The foams can for example be manufactured by a method similar to that described by Schwartzwalder et al. in US 3,090,094. They can also be purchased from commercial suppliers such as Drach Umwelttechnik GmbH (Diez, Germany), Céramiques Techniques et Industrielles s.a. (Salindres, France) or Selee Corporation (Hendersonville, North Carolina, USA). The foam substrates may be used in the form of monoliths or smaller pellets for fixed bed reactors.

The void fraction in the reactor bed is in range of 0.40 to 0.95, preferably in the range of 0.5 to 0.9. The total void fraction is composed of the open volume inside the foam together with the open volume between the pellets. A preferable range for the total void fraction is 0.45 to 0.95. The choice of combination of pore density and void fraction is determined by the required conversion for a given bed together with the maximum allowable pressure drop.

A platinum load of the monoliths of approximately 54.4 $g.ft^{-3}$ is used in a preferred embodiment of this invention.

An embodiment of the invention is the process where the reticulated foam is wash-coated with a high surface area oxide comprising of one or more metal oxides such as titania (TiO_2), zirconia (ZrO_2) or silica (SiO_2). After application of the high surface area wash coat, the catalytically active material platinum is introduced. The platinum can be introduced either by conventionally impregnation techniques or by chemical vapour deposition.

An embodiment of the invention is the process which uses a macroporous monolithic foam based catalyst. The foam is wash coated with a high-surface area oxide, thereby ensuring a high dispersion of the catalytically active phase, platinum.

A further embodiment of the invention comprises the process where the total void fraction of the catalyst is composed of the open volume inside the foam together with the open volume between the pellets is in the range of 0.45 to 0.95. Catalyst in the form of foam pellets and having the above

total void fraction is suitable for placement in a fixed bed reactor.

The catalyst, thus obtained, is suitable for catalytic oxidation of SO_2 to SO_3 and can be used in all the reactor beds.

Example 1

Three catalysts were made. Catalyst No. 1 was made from ceramic foam (20 PPI, zirconia-alumina) obtained from Céramiques Techniques et Industrielles s.a. (Salindres, France) was wash coated with an aqueous suspension of TiO_2 made by suspending 80g TiO_2 powder in a mixture of 70g TiO_2 sol, 30g water and dispersing agents. After drying at room temperature, the sample was calcined in air at 600°C. The wash coated reticulated foam was used as cylinders, 10 mm in diameter and 20 mm in length, impregnated with Pt using an aqueous solution of $[Pt(NH_3)_4](NO_3)_2$, dried and calcined at 600°C.

Catalyst No. 2 was made by impregnation of a 9 mm Daisy shaped ring of TiO_2 (surface area 70 m^2/g with the same Pt precursor).

Catalyst No. 3 was made according to Monsanto's method described in US patent No. 5,175,136.

The catalyst compositions and platinum loads are shown in Table 1.

Table 1

Catalyst No.	1	2	3
Carrier	TiO_2/α-Al_2O_3 foam	TiO_2	Al_2O_3/SiO_2/Mullite
Shape	10 mm pellets	9 mm Daisy rings	Honeycomb substrate
gram Pt/gross liter catalyst	0.19	1.13	1.92

These catalysts were loaded in the first, third and fourth beds of a reactor and the activity, expressed in terms of the conversion and rate constant, for SO_2 oxidation to SO_3 at different conditions was measured. The oxidation process utilising catalyst No. 1 illustrates the process of the invention. Oxidation processes utilising catalysts Nos. 2 and 3 are comparative. All conversions were measured at 400°C and are shown in Table 2.

Table 2

First bed: Conditions: 10.19% SO_2, 10% O_2, balance N_2, NHSV=16000 h^{-1}			
Catalyst No.	1	2	3
Conversion	5.4 %	37.37 %	35.11 %
Rate constant	888 $Nm^3/h/m^3$	7487 $Nm^3/h/m^3$	6920 $Nm^3/h/m^3$
Rate/Pt load	3552 /h/g/l	6626 /h/g/l	3604 /h/g/l
Third bed: Conditions: 1.966% SO_2, 7% O_2, balance N_2, NHSV=19400 h^{-1}			
Catalyst No.	1	2	3
Conversion	23.32 %	51.32 %	57.52 %
Rate constant	5151 $Nm^3/h/m^3$	13966 $Nm^3/h/m^3$	16609 $Nm^3/h/m^3$
Rate/Pt load	20604 /h/g/l	12359 /h/g/l	8651 /h/g/l
Fourth bed: Conditions: 0.757% SO_2, 7% O_2, balance N_2, NHSV=14700 h^{-1}			
Catalyst No.	1	2	3
Conversion	49.43 %	68.20 %	77.75 %
Rate constant	10023 $Nm^3/h/m^3$	16842 $Nm^3/h/m^3$	22092 $Nm^3/h/m^3$
Rate/Pt load	40092 /h/g/l	14904 /h/g/l	11506 /h/g/l

Dividing the rate constant with the platinum load (rate/Pt load) gives a number for the utilization of the platinum. Clearly the use of foam utilizes the platinum far better than a monolithic catalyst in third and fourth bed in accordance with the invention. For first bed the utilization is at the same level as a monolithic catalyst both being below a pellet catalyst.

Example 2

The pressure drop over a pellet bed with a length of 0.33 m and a diameter of 0.0855 m was measured as a function of different air flow rates at room temperature. The void fraction was calculated by weighing and measuring the amount of dry sand filling the interstices between the pellets constituting the bed.

The pellets used for this example were extrudates of a commercial SO_2 oxidation catalyst of the type VK-69, 9 mm daisy, obtained from Haldor Topsøe A/S, and crushed and sieved pellets of 10 PPI TiO_2 foam obtained from Céramiques Techniques et Industrielles s.a., Salindres, France. The specific area for foam particles was estimated from the geometric area of the foam and the measured void fraction. A specific area of 3000 m^2/m^3 and a void of 0.85 were used for the un-crushed foam. The specific area was measured for the commercial SO_2 oxidation catalyst. The values are given in Table 3.

Table 3

Pellet type	Size	Void	Specific area	Pressure drop at 0.94 m/s
-	Mm	-	m^2/m^3	kPa/m
Extrudates	9	0.55	575	1.65
Foam pellets	9	0.80	4000	0.42
Foam pellets	2-4.75	0.55	9000	2.32

The pressure drop as a function of linear velocity for different pellet types is shown in Fig. 1. The figure shows a

graph of the pressure drop as a function of linear air velocity through a fixed bed of different particles.

It is seen that by altering the foam pellet size distribution it is possible to vary the bed void fraction. Thus, with the same initial size of the reticulated foam pellets it is possible to obtain lower as well as higher pressure drops compared to a commercial SO_2 oxidation catalyst.

This is in accordance with the theory of flow through a fixed bed [R.B. Bird, W.E. Stewart and E.N. Lightfoot, Transport Phenomena, John Wiley & Sons, 1960]. Lowering the void results in higher pressure drop. On the other hand more active material per unit volume is placed in the catalyst bed. Using foam pellets of different size it is thus possible to optimize the acceptable pressure drop at a given flow rate towards the desire to have a certain catalytic activity per unit volume.

Furthermore, it is seen from Table 3 that a much lower pressure drop is obtained for large foam particles than for the extrudates even though the specific area per reactor volume is much larger. For film diffusion limited reactions, as is the case here, this is a great improvement to prior art.

CLAIMS

1. A process for the catalytic oxidation of sulphur dioxide to sulphur trioxide comprising contacting SO_2 under oxidation conditions with a catalyst comprising a reticulated ceramic foam having at its surface a wash coated layer of high surface area oxide serving as carrier for the active catalytic material platinum.

2. A process according to claim 1, wherein the reticulated ceramic foam is composed of α-alumina.

3. A process according to claim 2, wherein the wash coated layer comprises titania, zirconia or silica.

4. A process according to claims 1, 2 or 3, wherein the catalyst is in the form of foam pellets.

5. A process according to claims 1, 2 or 3, wherein the catalyst is monolithic.

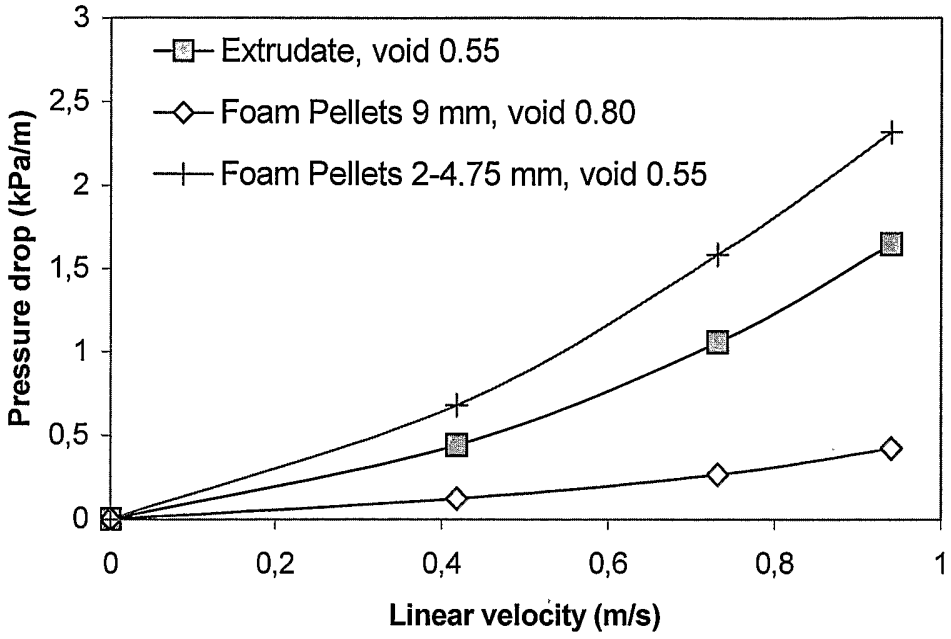
6. A process according to claim 4, wherein the foam pellets are in a fixed bed reactor.

7. A process according to claim 4, wherein the total void fraction composed of the open volume inside the foam together with the open volume between the pellets is in the range of 0.45 to 0.95.

8. Catalyst for the oxidation of sulphur dioide to sulphur trioxide comprising a reticulated ceramic foam having at its surface a wash coated layer of high surface area oxide serving as carrier for the active catalytic material platinum.

9. Catalyst according to claim 8, wherein the reticulated ceramic foam is composed of α-alumina.

10. Catalyst according to claims 8 or 9, wherein the wash coated layer comprises titania, zirconia or silica.


Extrudate, void 0.55
Foam Pellets 9 mm, void 0.80
Foam Pellets 2-4.75 mm, void 0.55
Pressure drop (kPa/m)
Linear velocity (m/s)
0
0,5
1
1,5
2
2,5
3
0
0,2
0,4
0,6
0,8
1

Figure