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WO-A-98/28073
WO-A-2006/009453
WO-A-2008/090450
GB-A- 2 406 802
US-A1- 2008 075 655
US-B1- 6 451 278

DESCRIPTION

[0001] The present invention relates to an ammonia oxidation catalyst unit formed of a pair of honeycomb-type blocks comprising an ammonia oxidation catalyst and having interplaced between them a layer of foamed material.

[0002] For many years, the catalysts for ammonia oxidation have been formed of meshes or gauzes of platinum or its alloy with other precious metals.

[0003] Such catalysts have good activity and selectivity but suffer from the disadvantage that the catalyst is not only very expensive but also it exhibits an appreciable loss of platinum at the high temperatures of the oxidation reaction with consequent low catalyst life, which requires frequent replacement.

[0004] It is therefore desirable to provide a replacement of such precious metal catalyst.

[0005] It is well known that oxides of metals such as manganese, iron, nickel or, especially cobalt, often used in conjunction with one or more rare earth metal oxides, exhibit activity for ammonia oxidation.

[0006] CN-A-86/108 985 describes a catalyst composition of formula $La_{1-x}CeCoO_3$ (where x is a number from 0 to 1) having perovskite structure, endowed with good activity and selectivity when tested on small scale, which decreases when operating at temperatures (800° - 1000°C) normally employed for ammonia oxidation.

[0007] US P 4 963 521 describes an exhaust gas catalyst which, in one embodiment, is formed of honeycomb cordierite coated with a first layer of gamma alumina mixed with minor proportion of zirconia and ceria, and a second layer formed of cobalt oxide or platinum, rhodium and palladium.

[0008] No mention is made that the catalyst can be used for oxidizing ammonia.

[0009] US P 5 217 939 describes an ammonia oxidation catalyst obtained by coating a reticulated foamed ceramic or metal substrate with cobalt oxide or with a noble metal.

[0010] The coating is obtained by immersion of the foamed substrate in a solution of a carboxylate of cobalt, or of a noble metal, removing the substrate from the solution and calcinating at temperatures from 260° to 800°C (at which the cobalt carboxylate is converted into oxide and the carboxylate of the noble metal is reduced to the metal).

[0011] The ceramic foams have a number of pores per linear inch of 10 to 100 (4 - 40/cm); 30 pores in the examples.

[0012] The conversion of ammonia to NO using the foam-Co oxide coated is 92-95%; using the foam coated with Pt 97-100%.

[0013] Further processing is necessary to convert nitric oxide (NO to NO₂) and then to nitric acid.

[0014] More efficient and economical catalysts in the production of nitric acid are therefore needed.

[0015] More efficient catalysts producing relatively high yields of NO₂ are described in US P 5 690 900. The catalysts are formed of porous ceramic (200 - 600 cells per square inch i.e. 14 - 24 cells per linear inch = 5 - 9 cells/cm) coated with at least three layers: the first is formed of alumina with minor proportion of ceria and zirconia, the second of oxides of cobalt, zirconium and cerium, the third of platinum metal.

[0016] The layers are obtained by immersing the porous ceramic body in a suspension of alumina, zirconium oxide and cerium nitrate, removing the impregnated ceramic structure and calcinating at 600° to 1000°C.

[0017] The resulting surface area is 80 - 120 m²/g.

[0018] The thus coated ceramic is then immersed in a solution of cobalt acetate, cerium nitrate and zirconium acetate, removed from the solution, and calcinated at 600 - 1000°C.

[0019] The last layer is obtained by immersion in a solution of platinum oxalate, and calcination at 600 - 1000°C of the structure

removed from the solution of the previous treatment. The ammonia conversion to NO/NO₂ is 95-100% with NO/NO₂ ratio of 75/25 to 60/40.

[0020] US 4 820 678 describes honeycomb-like alloy tapes coated with a catalyst having the perovskite (ABO₃) or spinel (A₂BO₄) structure, wherein A comprises cations of rare earth metal, B, in the perovskite structure, is selected from manganese, copper and nickel cations, in the spinel structure is selected from iron and nickel.

[0021] The catalyst is used for the purification of industrial waste gases, exhaust gases from automobiles, and purification of air.

[0022] The honeycomb tapes are obtained by perforating Fe - Cr - Al or Fe - Ni - Al alloy strips of about 0.05-0.12 mm thickness at distance of about 1.1-1.2 mm apart to form small holes of 0.4x0.4 mm.

[0023] US 6 451 278 describes a two-stage catalytic system for catalytic oxidation of ammonia, in which the first stage is a layer of platinoid nettings and the second stage is a layer pack comprising 2-5 space separated honeycomb blocks of catalytic structure, wherein - but not necessarily - a gas-permeable inert material is inserted between the blocks (in the examples a Ni-Cr netting 1.5 or 2 mm high is used).

[0024] The task performed by the 2-5 honeycomb blocks is to reduce the substantial loss of platinoids which occurs in the course of all processes of high-temperature conversion of ammonia, carried out with platinoid nettings. Thus, a longer service life of the catalytic system and, consequently, an increased yield of the desired product is obtained.

[0025] No mixing of the flow of gas occurs prior entering into the honeycomb blocks; the mixing of the flow of gas passing through the Ni-Cr netting can be considered negligible.

[0026] In example 3, wherein no Ni-Cr netting is used but a distance of 5 mm between the blocks is set up without using space regulators, the total conversion of ammonia is 98,1%, 94,3% of which is due to the stage using the platinoid nettings, the remainder is due to the honeycomb stage, wherein the conversion of ammonia is 67,3%. This results shows that the use of the 2-5 space separated honeycomb blocks as the only catalyst, without the platinoid nettings results in a low percentage of conversion of ammonia.

OBJECTS

[0027] It is an object of the present invention to provide ammonia oxidation catalysts comprised in honeycomb-type structures (wherein, due to their tubular structure, no radial gas flow mixing occurs and therefore no satisfactory conversion of the reagents) capable of giving high catalyst performance in terms of activity and selectivity and high specific productivity referred to the volume of the honeycomb structure bed and the weight of the catalyst.

DESCRIPTION OF THE INVENTION

[0028] The present invention is defined as per appended claims 1-13.

[0029] The catalysts for ammonia oxidation of the present invention are formed of one or more catalytic units each of which formed of a pair of blocks having honeycomb-type structure comprising an ammonia oxidation catalyst, each of said blocks having interplaced between them a layer performing the function of uniformly mixing the reagent gas flow.

[0030] The blocks have height of less than 15 cm and more than 2 cm, preferably the height is not more than 10 and more preferably not more

[0031] than 6 cm. The height of the interplaced layer is more than 0.5 cm and not more than 3 cm, preferably not more than 2 cm, and is formed of foamed material having open, randomly connected cells.

[0032] For honeycomb-type structure it is meant a structure formed of tubular not interconnected through bores. As indicated, in the above structure the interplaced layer performs the function of thoroughly mixing the gas flow exiting the first honeycomb block wherein, due to laminar piston-type flow inside the tubular not interconnected through bores, no radial mixing occurs, thus allowing better conversion inside the second block.

[0033] The laminar piston-type flow inside the tubular through bores of the blocks favors the maintenance of constant reagents concentration at contact with the catalyst covering the walls of the through bores.

[0034] The material of honeycomb-type block preferably is ceramic or metallic; any other material resistant to the high temperatures of the ammonia oxidation reaction can also be used. For example, the material of the honeycomb type block can be a perovskite of the ABO_3 type wherein A is a rare earth-element or an alkaline-earth element or mixtures thereof and B is a transition metal element or mixtures thereof.

[0035] In an embodiment, the density of the cells of the honeycomb blocks can range from 3 to 10 cells/cm; the density of the pores of the foamed material can be of 4 to 20 pores/cm.

[0036] Commercial honeycomb-type blocks are available from Emitech-Germany; commercial foams from Hi-Tech Ceramics - NY, USA.

[0037] Foamed alpha alumina and reticulated foams with open cells randomly connected are preferred. Usable honeycomb-type alloy blocks can also be obtained from tapes prepared according to US P 4 820 678.

[0038] Any type of ammonia oxidation catalyst can be used in the honeycomb-type structure unit according to the invention. The final catalyst can be obtained by either

1. a) coating an inert honeycomb monolithic structure with the active element or
2. b) extruding the active element powder to a honeycomb monolithic type structure.

[0039] A preferred catalyst comprises mixed oxides of cobalt, manganese and rare earth metals having composition expressed as percentage by weight of CoO, MnO and rare earth oxide in the lowest state of valence as follows: 20-45% CoO, 50-60% MnO, 0.5-20% rare earth metal oxide, preferably La_2O_3 and its mixtures with CeO_2 . The mixed oxides are supported on porous inorganic metal oxides, preferably gamma alumina. Catalysts of this type containing CuO in place of CoO, and the preparation thereof are described in WO 2008-090450.

[0040] Examples of other usable catalysts are described in US P 5 217 939 and 5 690 900, and WO 99/25650. Other examples are the perovskite type catalyst (ABO_3) and the spinel type (AB_2O_4).

[0041] The catalyst unit allows to obtain high conversion of ammonia to NO.

[0042] The oxidation reaction conditions are: temperature from 200°C to 900°C, pressure 1 to 12 bar abs., GHSV 8.000-100.000 h^{-1} .

[0043] The unit, thanks to its specific structure offers advantages with respect to the back pressure and increases the space-time yield since the throughput of the existing plants can be more heavily loaded.

EXAMPLE 1

[0044] A catalyst unit formed of three units of honeycomb-like structure ceramic blocks each having 5 cm height, 62 cells/cm² and including two layers of foamed alpha alumina each 2 cm thick interplaced by alternating one block of monolith and one foam until the five structures are arranged in cascade, was prepared by immersing the blocks in a slurry containing gamma alumina milled to 1 to 10 μm having supported on it a mixed oxides catalyst of composition expressed in percentage by weight of CoO, MnO and La_2O_3 of 37.4% CoO, 53.4% MnO and 9.2% La_2O_3 . The supported catalyst comprised also Pt in amount of 0.1 - 0.2 wt%. Said transition metal oxides are supported on gamma alumina in a global amount equal to 20% by weight. The slurry is further composed of deionized water and made acidic to pH 4 with acetic acid.

[0045] The catalyst was prepared by impregnating gamma alumina with an aqueous solution of lanthanum nitrate ($La(NO_3)_3$).

[0046] The impregnated support was then dried at 110°C, calcined at 600°C and thereafter impregnated with an aqueous

solution of manganese nitrate ($Mn(NO_3)_2$), cobalt nitrate ($Co(NO_3)_2$) and $Pt(NH_3)_4 Cl_2$, and dried at $120^\circ C$.

[0047] A volume of solution equal to 100% of the pore volume of alumina was used for impregnation.

[0048] The immersed blocks were removed from the slurry and calcinated at $500^\circ C$ to obtain reduction of platinum ions to metal.

[0049] The thus obtained unit was inserted into a reactor for ammonia oxidation. The reaction conditions were: GHSV = 10.000 h^{-1} , temperature of the gas mixtures taken at the inlet of the catalyst unit $550^\circ C$, pressure 1 bar and ammonia concentration equal to 1% v/v in air.

[0050] The conversion of ammonia to NO was higher than 96%.

COMPARISON EXAMPLE 1

[0051] A catalyst unit similar to that used in Example 1, but not comprising the foamed alumina layers, was used in a test of ammonia oxidation carried out under the same conditions as in Example 1.

[0052] The conversion of ammonia to NO was 87%.

COMPARISON EXAMPLE 2

[0053] A catalyst unit formed of a single honeycomb-like structure ceramic block having 15 cm height, 62 cells/cm² was prepared according to the procedure already described in the EXAMPLE 1 and was used in a test of ammonia oxidation carried out under the same conditions as in Example 1.

[0054] The conversion of ammonia to NO was 74%.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- [CN86106985A \[0006\]](#)
- [US4963521P \[0007\]](#)
- [US5217939P \[0009\]](#)
- [USP5690900P \[0015\]](#)
- [US4820678A \[0020\]](#)
- [US6451278S \[0023\]](#)
- [USP4820678P \[0037\]](#)
- [WO2008090450A \[0039\]](#)
- [USP5217939P \[0040\]](#)
- [US5690900P \[0040\]](#)
- [WO9925860A \[0040\]](#)

Patentkrav

1. Katalysatorer til ammoniakoxidation dannet af en eller flere katalytiske enheder, hvoraf hver af dem er dannet af et par af blokke, der har en honeycomb-struktur og omfatter en ammoniakoxidationskatalysator, hvor hver af
5 blokkene har en højde på mindre end 15 cm og mere end 2 cm, og der imellem dem er placeret et lag, som udfører den funktion, at det blander reagensgasstrømmen ensartet, med en højde på mere end 0,5 cm og ikke mere end 3 cm, dannet af skummateriale med åbne, vilkårligt forbundne celler.
- 10
2. Katalysatorenhed ifølge krav 1, hvor det mellemliggende skumlag har en højde på 0,5-2 cm.
3. Katalysatorenhed ifølge krav 1 eller 2, hvor højden af hver af blokkene er
15 fra 2 til 6 cm.
4. Katalysatorenhed ifølge et af kravene 1 til 3, hvor massefylden af cellerne i honeycomb-blokkene ligger i området fra 3 til 10 celler/cm, og massefylden af porerne i skumaterialet er fra 4 til 20 porer/cm.
- 20
5. Katalysatorenhed ifølge et af kravene 1 til 4, hvor blokkene er dannet af keramisk eller metallisk materiale.
6. Katalysatorenhed ifølge et af kravene 1 til 5, hvor det keramiske materiale
25 af blokkene med honeycomb-struktur har en Perowskit-struktur af ABO_3 -typen, hvor A er et sjældent jordartselement eller blandinger deraf, og B er et overgangsmetalelement eller blandinger deraf.
7. Katalysatorenhed ifølge et af kravene 1 til 6, hvor blokkene har et antal
30 celler pr. cm, hvilket kan være det samme eller forskelligt for hver af blokkene i katalysatorenheden, fra 3 til 10, og hvor antallet af porer pr. ca. i skumlaget

er 4 til 20.

8. Katalysatorenhed ifølge et af kravene 1 til 7, hvor skumlaget er dannet af opskummet aluminium.

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9. Katalysatorenhed ifølge krav 1 til 8, hvor ammoniakoxideringskatalysatoren foreligger i form af en coating opnået ved at dyppe blokkene i en opslæmning indeholdende gamma-aluminium med en på denne aflejret katalysator af blandede oxider med en sammensætning udtrykt i vægtprocent af
10 CoO, MnO og sjældne jordartsmetaller i det laveste valensstadium på 20-45 % CoO, 50-60 % MnO og 0,5-20 % oxider af sjældne jordartsmetaller, fjerne blokkene fra opslæmningen og kalcinere dem.

10. Katalysatorenhed ifølge krav 7, hvor det sjældne jordartsmetaloxid er
15 La₂O₃ og blandinger deraf med CeO₂.

11. Katalysatorenhed ifølge krav 7, hvor den katalysatorcoating, der er til stede på blokkene, omfatter 0,001-1 vægtprocent Pt.

12. Fremgangsmåde til ammoniakoxidation, hvor den anvendte katalysator er
20 dannet af en eller flere katalysatorenheder ifølge et af kravene 1 til 8.

13. Fremgangsmåde til ammoniakoxidation ifølge krav 12, udført ved temperaturer fra 200 °C til 900 °C, et tryk på 1 til 12 bar abs. og GHSV fra 8.000 to
25 100.000 h⁻¹.