

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

(19) World Intellectual Property
Organization

International Bureau

(43) International Publication Date
03 May 2018 (03.05.2018)



(10) International Publication Number
WO 2018/077554 A1

(51) International Patent Classification:

B01D 53/86 (2006.01)

(21) International Application Number:

PCT/EP2017/074368

(22) International Filing Date:

26 September 2017 (26.09.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

PCT/EP2016/076152

28 October 2016 (28.10.2016) EP

17168721.3 28 April 2017 (28.04.2017) EP

(71) Applicant: CASALE SA [CH/CH]; Via Giulio Pocobelli
6, 6900 Lugano (CH).

(72) Inventor: GRANGER, Jean François; Via Sorengo 17,
6900 Lugano (CH).

(74) Agent: ZARDI, Marco; c/o M. ZARDI & Co SA, Via Pi-
oda, 6, 6900 Lugano (CH).

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,
KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))

(54) Title: A METHOD FOR REMOVING NITROGEN OXIDES FROM A GAS USING AN IRON EXCHANGED ZEOLITE CATALYST

(57) Abstract: A method for removing nitrogen oxides NO_x from a gaseous current, comprising the steps of: passing the gaseous current through a de-NO_x catalytic bed with iron exchanged zeolite as a catalyst with the addition of ammonia as a reducing agent, wherein the molar ratio of NH₃ over NO_x is greater than 1.33.



A METHOD FOR REMOVING NITROGEN OXIDES FROM A GAS
USING AN IRON EXCHANGED ZEOLITE CATALYST

DESCRIPTION

Field of the invention

- 5 The invention relates to systems for removing nitrogen oxides from a gas.

Prior art

Removal of nitrogen oxides (NO_x) from a gas is of interest for environmental reasons. The flue gas of a combustion process typically contains NO_x due to nitrogen and oxygen in the oxidant air reacting at the high temperature of combustion. A further case of interest is the removal of NO_x from the tail gas of nitric acid production. Typically, in the nitric acid production, the tail gas denotes the gaseous current withdrawn from an absorption column where NO_x is absorbed into water to produce nitric acid. The tail gas contains residual amounts of NO_x which must be removed before the gas can be discharged.

A known measure to remove NO_x from a gaseous current is passing the NO_x-containing gas through a suitable catalytic bed with ammonia as a reducing agent. In the presence of ammonia, the nitrogen oxides are catalytically reduced to N₂ and H₂O.

20 The addition of ammonia needs be carefully regulated to reach a target removal of NO_x while avoiding ammonia slip, i.e. that some ammonia escapes the catalytic bed. A content of ammonia in the output gas leaving the catalytic bed is undesirable, especially if the effluent gas of the catalytic bed is then discharged to atmosphere. The permissible content of ammonia in a gas discharged into atmosphere is generally very low, for example 5 ppm. In some countries, release of ammonia into atmosphere may be

subject to a penalty fee.

Ammonia slip may also lead to formation of undesirable compounds such as ammonium nitrite or nitrate which can damage downstream equipment. For example the tail gas of nitric acid production is under pressure and is generally sent to an expander after removal of NO_x. The above compounds may damage the expander.

Summary of the invention

It has been surprisingly found that ammonia slip is unexpectedly low, or negligible, when a NO_x-containing gaseous current is passed through a de-NO_x catalytic bed, wherein the catalytic bed comprises iron-exchanged zeolite catalyst and the molar ratio of NH₃ over NO_x in the gas admitted to the catalytic bed is relatively high, being greater than 1.33.

Accordingly, an object of the present invention is a method for removing NO_x from a gaseous current according to claim 1. Preferred embodiments are disclosed in the dependent claims.

The term NO_x denotes collectively NO and NO₂.

The iron-exchanged zeolite catalyst, also termed iron-laden zeolite catalyst, is preferably any of: MFI, BEA, FER, MOR, FAU, MEL, or a combination thereof. Preferably, said iron exchanged zeolite is of the Fe-ZSM-5 type.

Preferably said ratio of NH₃ over NO_x is greater than 1.4, more preferably being 1.4 to 2, more preferably 1.4 to 1.6, even more preferably about 1.5. Preferred values include any of: 1.4, 1.45, 1.5, 1.55, 1.6.

After the passage through said de-NO_x catalytic bed, the residual amount of NO_x in the gas is preferably not greater than 100 ppm, preferably not greater than 50 ppm, more preferably not greater than 25 ppm. The term

ppm denotes parts per million in volume.

In a preferred embodiment, said de-NO_x catalytic bed is operated at a temperature in the range of 400 to 450 °C, preferably 430 °C or around 430 °C. Preferred working temperatures of the catalytic bed include: 420 °C,
5 425 °C, 430 °C, 435 °C.

The space velocity in said de-NO_x catalytic bed is preferably 10000 h⁻¹ to 14000 h⁻¹, preferably 10000 to 13000 h⁻¹ and more preferably 13000 h⁻¹.

In some embodiments the NO_x-containing gas is under pressure. In some embodiments the absolute pressure of the gas in said de-NO_x catalytic bed
10 is greater than 1 bar, preferably greater than 2 bar, more preferably 2 to 25 bar, even more preferably 5 to 15 bar.

The NO_x-containing input gaseous current can be a flue gas of a combustion process, or a tail gas of a process for making nitric acid, namely a gas withdrawn from an absorption column. Removing
15 environmental hazardous compounds from such tail gas (downstream of absorption column) is also termed tertiary abatement in contrast with primary and secondary abatement which are performed upstream the absorption column, or quaternary abatement which is performed after a subsequent expansion of the tail gas through an expander.

20 In an embodiment, the method of the invention does not comprise passing the NO_x-containing gas (e.g. combustion flue gas or tail gas of nitric acid production) through a de-N₂O catalytic bed before the passage through said de-NO_x catalytic bed.

In an embodiment, the method of the invention does not comprise passing
25 the NO_x-containing gas (e.g. combustion flue gas or tail gas of nitric acid production) through a series of a further de-NO_x catalytic bed and a

subsequent de-N₂O catalytic bed before the passage through said de-NO_x catalytic bed.

The NO_x-containing gas, however, may be passed through a first de-NO_x catalytic bed and then into said de-NO_x catalytic bed. An embodiment of the method of the invention includes: passing the NO_x-containing gas through a first de-NO_x catalytic bed, adding ammonia as a reducing agent to the effluent of said first-de-NO_x catalytic bed until the molar ratio of NH₃ over NO_x in said effluent gas is greater than 1.33, preferably 1.4 to 1.6, passing the effluent gas and ammonia directly through said de-NO_x catalytic bed without a passage through a de-N₂O catalytic bed.

In some embodiments the ammonia can be pure or in the form of a reducing agent containing ammonia.

The catalytic bed of the invention can be contained in a suitable vessel and can be traversed with axial, radial or mixed axial/radial flow, according to different embodiments. More than one catalytic bed, if provided, can be arranged in the same pressure vessel or separate pressure vessels. More than one catalytic bed contained in a single pressure vessel can be arranged one above the other or concentrically.

The invention provides a certain excess ammonia in the de-NO_x catalytic bed, the amount of ammonia being more than 1.33 moles per mole of NO_x.

The applicant has found that, in a surprising manner, the combination of iron-laden zeolite catalyst and of the above NH₃ / NO_x ratio, particularly with an operating temperature of the catalyst around 430 °C, results in a virtual absence of ammonia slip, typically less than 1 ppm. At the same time, the nitrogen oxides are efficiently removed. Accordingly the invention provides a method which is able to meet the most stringent limits of NH₃ and NO_x for emission into atmosphere.

The invention will be now further elucidated with reference to a non-limitative example.

Detailed description

5 A NO_x-containing gas, which can be a combustion flue gas or a tail gas of nitric acid production, is passed through a de-NO_x catalytic bed with the addition of ammonia as a reducing agent and NH₃/NO_x ratio in the gas greater than 1.33.

10 The NO_x-containing gas may be admitted directly to said de-NO_x catalytic bed or, in some embodiments, can be subject to a preliminary treatment e.g. in another de-NO_x catalytic bed.

For example, a gas containing 200 ppm of NO_x and 10 ppm of N₂O, is passed through a de-NO_x iron-laden zeolite catalytic bed with a space velocity of 13000 h⁻¹ at a pressure of 7 bar (absolute) and a temperature of 430 °C. The gas is a tail gas of nitric acid production and further contains
15 3% oxygen and around 0.3% water. The NH₃/NO_x ratio was varied between 1.33 and 1.5.

Abatement of 99.4% NO_x was observed with a NH₃/NO_x ratio of 1.4 and 99.7% was observed with a NH₃/NO_x ratio of 1.5. The ammonia content of the effluent gas was below measurement level, i.e. no ammonia slip was
20 detected.

CLAIMS

1. A method for removing nitrogen oxides NO_x from a gaseous current, comprising the steps of:
 - 5 passing the gaseous current through a de-NO_x catalytic bed comprising a catalyst which is iron exchanged zeolite, with the addition of ammonia as a reducing agent,
wherein the molar ratio of NH₃ over NO_x in the gas admitted to said de-NO_x catalytic bed is greater than 1.33.
- 10 2. A method according to claim 1, said ratio of NH₃ over NO_x being greater than 1.4.
3. A method according to claim 2, said ratio of NH₃ over NO_x being 1.4 to 2, preferably 1.4 to 1.6, more preferably 1.5 or about 1.5.
4. A method according to any of the previous claims, wherein, after the
15 passage through said de-NO_x catalytic bed, the residual amount of NO_x in the gas is not greater than 100 ppm, preferably not greater than 50 ppm, more preferably not greater than 25 ppm.
5. A method according to any of the previous claims comprising the step of:
operating said de-NO_x catalytic bed at a temperature in the range of 400
20 to 450 °C, preferably 430 °C.
6. A method according to any of the previous claims, wherein the iron exchanged zeolite catalyst is chosen among the following types: MFI, BEA, FER, MOR, FAU, MEL, or a combination thereof.
7. A method according to claim 6, wherein the iron exchanged zeolite is of
25 the Fe-ZSM-5 type.

8. A method according to any of the previous claims, wherein the space velocity in said de-NOx catalytic bed is 10000 h⁻¹ to 14000 h⁻¹, preferably 13000 h⁻¹.
9. A method according to any of the previous claims, the absolute pressure of the gas in said de-NOx catalytic bed being greater than 1 bar, preferably 2 to 25 bar, more preferably 5 to 15 bar.
10. A method according to any of the previous claims wherein the gaseous current is a tail gas of a process for making nitric acid, withdrawn from an absorption column.
- 10 11. A method according to any of the previous claims comprising: passing the NOx-containing gas through a first de-NOx catalytic bed, adding ammonia as a reducing agent to the effluent of said first-de-NOx catalytic bed until the molar ratio of NH₃ over NOx in said effluent gas is greater than 1.33, preferably 1.4 to 1.6, passing the effluent gas and ammonia directly through said de-NOx catalytic bed without a passage through a de-N₂O catalytic bed.
- 15
12. A method according to any of the previous claims, wherein the gaseous current is a flue gas of a combustion process, or a tail gas of a process for making nitric acid withdrawn from an absorption column, and
- 20 the process does not comprise passing the gas through a series of another de-NOx catalytic bed and a subsequent de-N₂O catalytic bed, before the passage through said de-NOx catalytic bed.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/074368

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/86
ADD.
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)
B01D
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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/363359 A1 (SCHWEFER MEINHARD [DE] ET AL) 11 December 2014 (2014-12-11)	1-10
Y	paragraphs [0002], [0102], [0106], [0110], [0128], [0129], [0131]	1-12
X	US 4 571 329 A (KATO YASUYOSHI [JP] ET AL) 18 February 1986 (1986-02-18)	1-12
Y	claims 1, 2 column 5, line 57 - line 63 column 8; example 10 figures 4, 5, 6	1-12
X	US 2002/039550 A1 (SCHAFER-SINDLINGER ADOLF [DE] ET AL) 4 April 2002 (2002-04-04)	1-4,6-9, 11
A	figure 1 claims 1-5 paragraphs [0035] - [0037]	10
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search 21 February 2018	Date of mailing of the international search report 05/03/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Pöhlmann, Robert

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/074368

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	claim 16 paragraph [0073]; table 1 paragraphs [0001], [0002], [0064], [0066], [0067], [0069], [0074] -----	11
Y	US 2003/143141 A1 (SCHWEFER MEINHARD [DE] ET AL) 31 July 2003 (2003-07-31) paragraphs [0001], [0019], [0042] - [0046], [0048], [0049] figure 1 claim 8 -----	1-12

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Information on patent family members

International application No

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