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EP 0373665 A2 **WO 2000/072965 A1**
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(54) Title of the Invention: **Transition metal-containing aluminosilicate zeolite**
Abstract Title: **Aluminosilicate zeolite catalyst and use thereof in exhaust gas after-treatment**

(57) A synthetic aluminosilicate zeolite catalyst containing at least one catalytically active transition metal selected from the group consisting of Cu, Fe, Hf, La, Au, In, V, lanthanides and Group VIII transition metals, which aluminosilicate zeolite is a small pore aluminosilicate zeolite having a maximum ring size of eight tetrahedral atoms, wherein the mean crystallite size of the aluminosilicate zeolite determined by scanning electron microscope is >0.50 micrometer. Also disclosed is use of the aluminosilicate zeolite catalyst in exhaust gas after-treatment.

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TRANSITION METAL-CONTAINING ALUMINOSILICATE ZEOLITE

The present invention relates to a synthetic aluminosilicate zeolite catalyst containing at least one catalytically active transition metal. The zeolites can be used for selective catalytic reduction (SCR) of nitrogen oxides in exhaust gases, such as exhaust gases from internal combustion engines, using a nitrogenous reductant.

It is known to convert oxides of nitrogen (NO_x) in a gas to nitrogen by contacting the NO_x with a nitrogenous reducing agent, e.g. ammonia or an ammonia precursor such as urea, in the presence of a zeolite catalyst containing at least one transition metal, and it has been suggested to adopt this technique for treating NO_x emitted from vehicular lean-burn internal combustion engines, see for example DieselNet Technology Guide "Selective Catalytic Reduction" Revision 2005.05d, by W. Addy Majewski published on www.dieselnets.com.

US patent no. 4,544, 538 discloses a synthetic zeolite having a crystal structure of chabazite (CHA), designated SSZ-13 prepared using a Structure Directing Agent (SDA) such as the N,N,N-trimethyl-1-adamantammonium cation. The SSZ-13 can be ion exchanged with transition metals such as rare earth, Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe and Co for use e.g. in hydrocarbon conversion reactions.

US patent no. 6,709,644 discloses a synthetic zeolite having a crystal structure of chabazite (CHA) of small crystallite size (on average <0.5 micrometers) designated SSZ-62. SSZ-62 can also be prepared using the N,N,N-trimethyl-1-adamantammonium cation SDA. Example 1 of US 6,709,644 compares the average crystal size of SSZ-62 with the average crystal size of SSZ-13. The document suggests that SSZ-62 can be used in a process for converting lower alcohols or the zeolite can be exchanged with copper or cobalt for use in catalysing the reduction of NO_x in a lean gas stream e.g. of an internal combustion engine. However, the activity of small and large crystallite size materials are only illustrated by a methanol to olefin reaction.

In our International patent application no. PCT/GB2008/001451 filed 24th April 2008 we explain that transition metal/zeolite catalysts such as Cu/Beta and/or Fe/Beta are being considered for urea and/or NH_3 SCR of NO_x from mobile diesel engines to meet new emission standards. These catalysts are required to withstand relatively high temperatures under exhaust conditions,

and may also be exposed to relatively high levels of hydrocarbons (HC), which can be adsorbed onto or into the pores of the zeolites. The adsorbed HC may affect the NH₃ SCR activities of these metal zeolites catalysts by blocking the active sites or blocking access to the active sites for the NH₃-NO_x reaction. Furthermore, these adsorbed HC species may be oxidised as the temperature of the catalytic system is raised, generating a significant exotherm, which can thermally or hydrothermally damage the catalyst. It is therefore desirable to minimise HC adsorption on the SCR catalyst, especially during cold start when significant amounts of HC can be emitted from the engine.

10 In our PCT/GB2008/001451 we suggest that both of these disadvantages of larger pore zeolite catalysts can be reduced or overcome by using small pore zeolites, which generally allow the diffusion of NH₃ and NO_x to the active sites inside the zeolite pores, but which generally hinder diffusion of hydrocarbon molecules into the pores. Zeolites that have the small pore dimensions to induce this shape selectivity whereby larger hydrocarbons are prevented from accessing the active metal sites within the zeolite cavities include CHA, ERI and LEV. Additionally, small pore
15 zeolite-based SCR catalysts produce less N₂O as a by-product of the NO_x reduction reaction.

We have researched into aluminosilicate zeolite materials and have discovered, very surprisingly, that large crystallite aluminosilicate zeolite materials have higher activity for the SCR process using a nitrogenous reductant than the same aluminosilicate zeolite material of smaller crystallite size.

According to one aspect, the invention provides a synthetic aluminosilicate zeolite catalyst containing at least one catalytically active transition metal selected from the group consisting of Cu, Fe, Hf, La, Au, In, V, lanthanides and Group VIII transition metals, which aluminosilicate zeolite is a small pore aluminosilicate zeolite having a maximum ring size of eight tetrahedral atoms, wherein the mean crystallite size of the aluminosilicate zeolite determined by scanning electron microscope is >0.50 micrometer. Preferably, the at least one catalytically active transition metal is one of copper and iron. In embodiments, the zeolite can contain both copper and iron.

The Examples show a trend of increasing NO_x reduction activity of fresh and aged copper/CHA catalysts with increasing crystallite size.

Scanning electron microscopy can determine the morphology and crystallite size of zeolites according to the invention. It is desirable that the mean particle size of the aluminosilicate zeolite as measured by SEM is >0.50 micrometer, but preferably greater than 1.00 micrometer, such as >1.50 micrometers. In embodiments, the mean crystallite size is <15.0 micrometers, such as
5 <10.0 micrometers or <5.0 micrometers.

In embodiments, the aluminosilicate zeolite catalyst according to the invention is selected from the group consisting of zeolites having a maximum ring size of eight tetrahedral atoms especially Framework Type Codes CHA, ERI and LEV, most preferably CHA.
10

Where the Framework Type Code of the aluminosilicate zeolite is CHA, an isotype framework structure of CHA can be selected from the group consisting of, for example, Linde-D, Linde-R, SSZ-13, LZ-218, Phi, ZK-14 and ZYT-6.

A type material or isotype framework structure of ERI Framework Type Code zeolites can be, for example, erionite, ZSM-34 or Linde Type T.
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LEV Framework Type Code isotype framework structures or type material can be, for example, levynite, Nu-3, LZ-132 or ZK-20.
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The total at least one transition metal present in the catalyst is from 0.1 to 10.0 wt% based on the total weight of the zeolite catalyst, such as 0.5 to 5.0 wt% based on the total weight of the zeolite catalyst.

According to another aspect, the invention provides a method of converting nitrogen oxides in a gas to nitrogen by contacting the nitrogen oxides with a nitrogenous reducing agent in the presence of an aluminosilicate zeolite catalyst according to the invention.
25

The nitrogen oxides can be reduced with the reducing agent at a temperature of at least
30 100°C, for example from about 150°C to 750°C.

In a particular embodiment, the nitrogen oxides reduction is performed in the presence of oxygen.

The addition of nitrogenous reductant can be controlled so that NH_3 at the zeolite catalyst inlet is controlled to be 60% to 200% of theoretical ammonia calculated at 1:1 NH_3/NO and 4:3 NH_3/NO_2 .

5 In a particular embodiment, wherein nitrogen monoxide in the gas is oxidised to nitrogen dioxide using an oxidation catalyst located upstream of the zeolite catalyst and the resulting gas is then mixed with nitrogenous reductant before the mixture is fed into the zeolite catalyst, wherein the oxidation catalyst is adapted to yield a gas stream entering the zeolite catalyst having a ratio of NO to NO_2 of from about 4:1 to about 1:3 by volume.

10

In the method according to the invention, the nitrogenous reductant can be ammonia *per se*, hydrazine or an ammonia precursor selected from the group consisting of urea $((\text{NH}_2)_2\text{CO})$, ammonium carbonate, ammonium carbamate, ammonium hydrogen carbonate and ammonium formate.

15

The gas containing nitrogen oxides to be treated with the method according to the present invention can be derived from a combustion process, particularly from an internal combustion engine such as a stationary source or preferably a vehicular lean burn internal combustion engine.

20

According to another aspect, the invention provides an exhaust system for a vehicular lean-burn internal combustion engine, which system comprising a conduit for carrying a flowing exhaust gas, a source of nitrogenous reductant, a synthetic aluminosilicate zeolite catalyst containing at least one catalytically active transition metal selected from the group consisting of
25 Cu, Fe, Hf, La, Au, In, V, lanthanides and Group VIII transition metals, which aluminosilicate zeolite is a small pore aluminosilicate zeolite having a maximum ring size of eight tetrahedral atoms, disposed in a flow path of the exhaust gas and means for metering nitrogenous reductant into a flowing exhaust gas upstream of the zeolite catalyst, wherein the mean crystallite size of the aluminosilicate zeolite determined by scanning electron microscope is >0.50 micrometer.

30

In order that the invention may be more fully understood, the following Examples are provided by way of illustration only.

Example 1 – Preparation of zeolite samples

Zeolite A

Small crystallite CHA was prepared according to Example 1 of US 6709644 (the entire contents of which is incorporated herein by reference).

5

Zeolite B

Large crystallite CHA was prepared according to a method of making SSZ-13 by S.I. Zones and R A. Van Nordstrand, Zeolites 8 (1988) 166 (the entire contents of which is incorporated herein by reference) also published on International Zeolite Association Synthesis Commission web-site <http://www.iza-online.org/synthesis/>, as follows:

10

The source materials were:

sodium hydroxide (1 N), (Baker, reagent grade);

N,N,N, trimethyl-1-adamantanammonium hydroxide (RN-OH)(0.72M);

15

deionized water;

aluminium hydroxide (Reheis F-2000 dried gel, 50% Al₂O₃); and

fumed silica (Cab-Q-Sil, M5 grade, 97% SiO₂).

The reaction mixture was prepared as follows:

20

(1) 2.00 g 1N NaOH + 2.78 g 0.72 M RN·OH + 3.22g water, add sequentially to a Teflon cup of a Parr 23 mL autoclave;

(2) (1) + 0.05 g aluminum hydroxide, mix until solution clears;

(3) (2) + 0.60 g fumed silica, mix until uniform.

25

The reaction mixture was crystallised:

in a teflon-lined 23 mL autoclave (Parr model 4745) at a temperature of 160°C for 4 days without agitation;

After cooling to room temperature the mixture was filtered, washed with de-mineralised water and air-dried overnight.

30

The resulting product was characterised by powder x-ray diffraction and identified as:

CHA zeolite with a SiO₂/Al₂O₃ ratio of 28 as determined by ICP.

SEM analysis showed:

cubes of 2-5 micrometers.

Zeolite C

5 A reaction mixture was prepared of molar composition $60 \text{ SiO}_2 - 1.5 \text{ Al}_2\text{O}_3 - 6 \text{ Na}_2\text{O} - 12 \text{ NNNAnOH} - 2640 \text{ H}_2\text{O}$, where NNNAnOH is the structure directing agent (SDA) or template N,N,N-trimethyladamantanammonium hydroxide

The reaction was prepared using cab-o-sil M5 (Cabot Corporation) as the source of silica,
10 sodium aluminate (BDH Ltd), sodium hydroxide (Alfa Aesar). The SDA (NNNAnOH) was prepared following the method described in US patent no. 4,544,538 (the entire contents of which is incorporated herein by reference). The required amount of the SDA solution was weighed out and the NaOH added and stirred until it dissolved. The sodium aluminate solid was then added with stirring and stirring was continued until it dissolved. The cab-o-sil was then
15 mixed in and the resulting mixture transferred to a 1L stainless steel autoclave. The autoclave was sealed and the mixture heated to 165C with stirring (300rpm) for 4 days.

The resulting product was identified as a CHA type material by powder x-ray diffraction. Visually, the product crystals were approximately 2 microns on edge. The product composition
20 had a silica-alumina ratio (SAR) of 24:1.

Example 2 – Preparation of 3wt%Cu/aluminosilicate zeolite

Copper was deposited on zeolites A, B and C prepared according to Example 1 by the
25 standard wet impregnation method using copper acetate as the copper precursor. For 10g of aluminosilicate zeolite, 0.471g of copper acetate was dissolved in a sufficient amount of water to wet the aluminosilicate zeolite material. The solution was added to the aluminosilicate zeolite material and stirred. The wet powder was dried at 105°C, before being calcined at 500°C for 2 hours. Following calcination, a majority of the copper is understood to be present as copper (II)
30 oxide.

The copper-loaded catalysts prepared according to this Example were designated as Catalysts A, B and C. Catalysts prepared according to Example 2 are referred to as "Fresh Catalysts A-C".

Example 3 – Hydrothermal Ageing

5 Fresh Catalysts A-C prepared according to Example 2 were hydrothermally aged in an atmosphere containing 10% oxygen, 10% water, balance nitrogen at 750°C for a period of 24 hours. The hydrothermally aged catalyst is referred to as “Aged Catalysts A-C”.

Table 1: surface area, silica alumina ratio, crystal size and copper loading of the different catalysts (fresh).

Chabazite Aluminosilicate code	BET surface area	Silica to alumina ratio (SAR)	Average SEM Crystal Dimension (micrometer)*	Cu loading wt%
A	784	26	0.15	3
B	634	24	0.5	3
C	616	24	1.4	3

10

* The samples were dispersed in methanol and subjected to ultrasound for 20 mins and a drop of this liquid was put on a standard carbon padded Scanning Electron Microscope (SEM) stub. Counting and sizing was determined by number averaged digital particle size analysis, based on “thresholding” the intensities from each pixel of an image, and exploiting the differences in
15 intensity between particles and the background. The software assumes that each object detected is circular/spherical.

Example 4 – Activity Tests

20

The NO_x conversion of Catalysts A-C of Examples 2 and 3 at an inlet gas temperature of 200°C or 400°C are given in Table 2. The NO_x reduction performance was measured on a powder sample in a laboratory reactor by ramping the catalyst at 5°C per minute in a gas mixture containing 500ppm NO and NH₃, 10%O₂, 10%H₂O and N₂.

25

Table 2: NO_x conversion at a catalyst inlet gas temperature of 200°C and 400°C for Fresh and 750°C 24 hour-Aged Conditions

Catalyst	SAR	Average SEM Crystal Dimension (micrometer) †	Cu Loading wt%	500°C Calcined % NO _x Conversion			750°C Aged % NO _x Conversion		
				190°C	200°C	400°C	190°C	200°C	400°C
A	26	0.15	3	73	86	99	44	58	96
B	24	0.5	3	85	95	99	51	66	97
C	24	1.4	3	87	97	99	68	83	99

† See notes on Table 1.

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It can be seen from Table 2 that the activity of the catalysts generally follows a trend of increasing activity with crystallite size. Hence we conclude that larger crystallite size aluminosilicate zeolite materials are surprisingly more active either fresh or hydrothermally aged than catalysts prepared from smaller crystals of the same aluminosilicate zeolite material.

CLAIMS:

1. A synthetic aluminosilicate zeolite catalyst containing at least one catalytically active transition metal selected from the group consisting of Cu, Fe, Hf, La, Au, In, V, lanthanides and Group VIII transition metals, which aluminosilicate zeolite is a small pore aluminosilicate zeolite having a maximum ring size of eight tetrahedral atoms, wherein the mean crystallite size of the aluminosilicate zeolite determined by scanning electron microscope is >0.50 micrometer.
5
2. An aluminosilicate zeolite catalyst according to claim 1, wherein the at least one catalytically active transition metal is copper, iron or copper and iron.
10
3. An aluminosilicate zeolite catalyst according to claim 1 or 2, wherein the at least one catalytically active transition metal consists of copper.
4. An aluminosilicate zeolite catalyst according to claim 1, 2 or 3, wherein the mean crystallite size is >1.00 micrometer
15
5. An aluminosilicate zeolite catalyst according to claim 1, 2, 3 or 4, wherein the mean crystallite size is >1.50 micrometers.
20
6. An aluminosilicate zeolite catalyst according to any preceding claim, wherein the mean crystallite size is <15.00 micrometers.
7. An aluminosilicate zeolite catalyst according to any preceding claim, wherein the aluminosilicate zeolite is selected from the group consisting of Framework Type Codes CHA, ERI and LEV.
25
8. An aluminosilicate zeolite catalyst according to any of claims 1 to 6, wherein the aluminosilicate zeolite is from the Framework Type Code CHA.
30
9. An aluminosilicate zeolite catalyst according to claim 7 or 8 wherein isotype framework structures of CHA are selected from the group consisting of Linde-D, Linde-R, SSZ-13, LZ-218, Phi, ZK-14 and ZYT-6.

10. An aluminosilicate zeolite catalyst according to claim 7, wherein a type material or isotype framework structures of ERI are erionite, ZSM-34 or Linde Type T.

5 11. An aluminosilicate zeolite catalyst according to claim 7, wherein a type material or isotype framework structures of LEV are levynite, Nu-3, LZ-132 or ZK-20.

12. An aluminosilicate zeolite catalyst according to any preceding claim, wherein the total at least one transition metal present in the catalyst is from 0.1 to 10.0 wt% based on the total weight of the zeolite catalyst.

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13. An aluminosilicate zeolite catalyst according to claim 12, wherein the total at least one transition metal present in the catalyst is from 0.5 to 5.0 wt% based on the total weight of the zeolite catalyst.

15 14. A method of converting nitrogen oxides in a gas to nitrogen by contacting the nitrogen oxides with a nitrogenous reducing agent in the presence of an aluminosilicate zeolite catalyst according to any preceding claim.

20 15. A method according to claim 14, wherein the nitrogen oxides are reduced with the reducing agent at a temperature of at least 100°C.

16. A method according to claim 15, wherein the temperature is from about 150°C to 750°C.

25 17. A method according to claim 14, 15 or 16, wherein the nitrogen oxides reduction is performed in the presence of oxygen.

18. A method according to claim 14, 15, 16 or 17, wherein addition of nitrogenous reductant is controlled so that NH_3 at the zeolite catalyst inlet is controlled to be 60% to 200% of theoretical ammonia calculated at 1:1 NH_3/NO and 4:3 NH_3/NO_2 .

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19. A method according to any of claims 14 to 18, wherein nitrogen monoxide in the gas is oxidised to nitrogen dioxide using an oxidation catalyst located upstream of the zeolite catalyst and the resulting gas is then mixed with nitrogenous reductant before the mixture is fed into the

zeolite catalyst, wherein the oxidation catalyst is adapted to yield a gas stream entering the zeolite catalyst having a ratio of NO to NO₂ of from about 4:1 to about 1:3 by volume.

20. A method according to any of claims 14 to 19, wherein the nitrogenous reductant is ammonia *per se*, hydrazine or an ammonia precursor selected from the group consisting of urea ((NH₂)₂CO), ammonium carbonate, ammonium carbamate, ammonium hydrogen carbonate and ammonium formate.

21. A method according to any of claims 14 to 20, wherein the gas containing nitrogen oxides is derived from a combustion process.

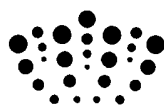
22. A method according to claim 21, wherein the combustion process is the combustion of fuel in a vehicular lean burn internal combustion engine.

23. An exhaust system for a vehicular lean-burn internal combustion engine, which system comprising a conduit for carrying a flowing exhaust gas, a source of nitrogenous reductant, a synthetic aluminosilicate zeolite catalyst containing at least one catalytically active transition metal selected from the group consisting of Cu, Fe, Hf, La, Au, In, V, lanthanides and Group VIII transition metals, which aluminosilicate zeolite is a small pore aluminosilicate zeolite having a maximum ring size of eight tetrahedral atoms, disposed in a flow path of the exhaust gas and means for metering nitrogenous reductant into a flowing exhaust gas upstream of the zeolite catalyst, wherein the mean crystallite size of the aluminosilicate zeolite determined by scanning electron microscope is >0.50 micrometer.

24. A synthetic aluminosilicate zeolite catalyst substantially as described herein with reference to the accompanying Examples.

25. A method of converting nitrogen oxides in a gas to nitrogen substantially as described herein with reference to the accompanying Examples.

26. An exhaust system for a vehicular lean-burn internal combustion engine substantially as described herein.



Application No: GB0818887.2

Examiner: Dr Albert Mthupha

Claims searched: 1-26

Date of search: 6 March 2009

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-6, 12-13, 16, 21-23, 26.	EP0373665 A2 (TOSOH), see whole document, note particularly page 2 lines 1-3, lines 28-32, lines 43-55, page 3 lines 19-20, lines 45-53, Examples 1-4, Claims 1-6.
X	1-7.	CA2224648 C (SHELL), see whole document, note particularly page 12 lines 17-24, page 13 line 16, Claims 1, 10, 15.
X	1-13.	US2002/0183192 A1 (VERDUIJN J.P. ET. AL.), see whole document, note particularly para. [0026], [0038]-[0039] (note use of copper & Group VIII transition metals), [0043], [0066], Claims 1, 4, 6-7, 19.
X	1, 4-11.	US4025571 A (MOBIL), see whole document, note particularly column 1 lines 42-53, column 4 lines 26-40, column 7 lines 55-61, column 8 lines 35-59.
X	1-2, 4-5, 12-15, 17, 19-23, 26.	WO00/72965 A1 (THE UNIVERSITY OF MICHIGAN), see whole document, note particularly page 1 lines 10-14, page 5 lines 5-6. liners 9-10, page 7 lines 18-19, page 9 line 32-page 10 line 3, page 13 lines 2-4 (note catalysts ground to 60-100 mesh (i.e. 250-149 microns), Claims 1, 3, 4, 17, 19, 20.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

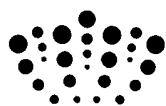
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Worldwide search of patent documents classified in the following areas of the IPC

B01D; B01J

The following online and other databases have been used in the preparation of this search report

ONLINE : EPODOC, WPI.



International Classification:

Subclass	Subgroup	Valid From
B01J	0029/72	01/01/2006
B01D	0053/94	01/01/2006
B01J	0029/56	01/01/2006
B01J	0029/70	01/01/2006
C01B	0039/48	01/01/2006