



- (51) International Patent Classification:
B01J 23/72 (2006.01) *B01J 29/06* (2006.01)
B01J 23/02 (2006.01)
- (21) International Application Number:
PCT/US2013/065501
- (22) International Filing Date:
17 October 2013 (17.10.2013)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/716,067 19 October 2012 (19.10.2012) US
14/056,431 17 October 2013 (17.10.2013) US
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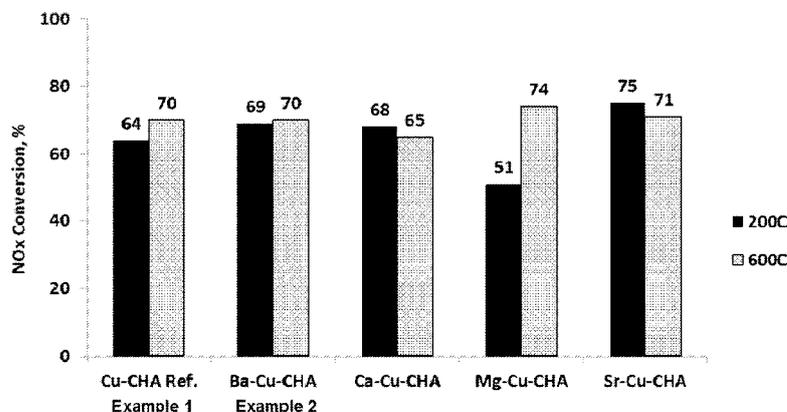
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, 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))

(54) Title: 8-RING SMALL PORE MOLECULAR SIEVE WITH PROMOTER TO IMPROVE LOW TEMPERATURE PERFORMANCE

Figure 5



(57) Abstract: Described is a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component. The catalyst is effective to catalyze the reduction of nitrogen oxides (NOx) in the presence of a reductant. A method for selectively reducing nitrogen oxides is also described.

WO 2014/062952 A1

8-RING SMALL PORE MOLECULAR SIEVE WITH PROMOTER TO
IMPROVE LOW TEMPERATURE PERFORMANCE

PRIORITY

This patent application claims priority to pending patent application Serial 61/716067 filed October 19, 2012 and Serial 14/056431 filed October 17, 2013.

TECHNICAL FIELD

[0001] The present invention pertains to the field of selective catalytic reduction catalysts. More specifically, the present invention relates to selective catalytic reduction catalysts comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component, and methods of using these catalysts in a variety of processes such as abating pollutants in exhaust gases.

BACKGROUND

[0002] Molecular sieves such as zeolites have been used extensively to catalyze a number of chemical reactions in refinery and petrochemical reactions, and catalysis, adsorption, separation, and chromatography. For example, with respect to zeolites, both synthetic and natural zeolites and their use in promoting certain reactions, including conversion of methanol to olefins (MTO reactions) and the selective catalytic reduction (SCR) of nitrogen oxides with a reductant such as ammonia, urea or a hydrocarbon in the presence of oxygen, are well known in the art. Zeolites are crystalline materials having rather uniform pore sizes which, depending upon the type of zeolite and the type and amount of cations included in the zeolite lattice, range from about 3 to 10 Angstroms in diameter. Zeolites having 8-ring pore openings and double-six ring secondary building units, particularly those having cage-like structures have recently found interest in use as SCR catalysts. A specific type of zeolite having these properties is chabazite (CHA), which is a small pore zeolite with 8 member-ring pore openings (~3.8 Angstroms) accessible through its 3-dimensional porosity. A cage like structure results from the connection of double six-ring building units by 4 rings.

[0003] Catalysts employed in the SCR process ideally should be able to retain good catalytic activity over the wide range of temperature conditions of use, for example,

200 °C to 600 °C or higher, under hydrothermal conditions. Hydrothermal conditions are often encountered in practice, such as during the regeneration of a soot filter, a component of the exhaust gas treatment system used for the removal of particles.

[0004] Metal-promoted zeolite catalysts including, among others, iron-promoted and copper-promoted zeolite catalysts, for the selective catalytic reduction of nitrogen oxides with ammonia are known. Iron-promoted zeolite beta has been an effective commercial catalyst for the selective reduction of nitrogen oxides with ammonia. Unfortunately, it has been found that under harsh hydrothermal conditions, for example exhibited during the regeneration of a soot filter with temperatures locally exceeding 700 °C, the activity of many metal-promoted zeolites begins to decline. This decline is often attributed to dealumination of the zeolite and the consequent loss of metal-containing active centers within the zeolite.

[0005] The synthesis of a zeolite varies according to structure type of the zeolite, but usually, zeolites are synthesized using a structure directing agent, sometimes referred to as a template or organic template) together with sources of silica and alumina. The structure directing agent can be in the form of an organic, i.e. tetraethylammonium hydroxide (TEAOH), or inorganic cation, i.e. Na^+ or K^+ . During crystallization, the tetrahedral silica-alumina units organize around the SDA to form the desired framework, and the SDA is often embedded within the pore structure of the zeolite crystals.

[0006] Metal-promoted, particularly copper promoted aluminosilicate zeolites having the CHA structure type and a silica to alumina molar ratio greater than 1, particularly those having a silica to alumina ratio greater than or equal to 5, 10, or 15 and less than about 1000, 500, 250, 100 and 50 have recently solicited a high degree of interest as catalysts for the SCR of oxides of nitrogen in lean burning engines using nitrogenous reductants. This is because of the wide temperature window coupled with the excellent hydrothermal durability of these materials, as described in United States Patent Number 7,601,662. Prior to the discovery of metal promoted zeolites described in United States Patent Number 7,601,662, while the literature had indicated that a large number of metal-promoted zeolites had been proposed in the patent and scientific literature for use as SCR catalysts, each of the proposed materials suffered from one or both of the following defects: (1) poor conversion of oxides of nitrogen at low

temperatures, for example 350° C and lower; and (2) poor hydrothermal stability marked by a significant decline in catalytic activity in the conversion of oxides of nitrogen by SCR. Thus, the invention described in United State Patent Number 7,601,662 addressed a compelling, unsolved need to provide a material that would provide conversion of oxides of nitrogen at low temperatures and retention of SCR catalytic activity after hydrothermal aging at temperatures in excess of 650° C.

[0007] Thus, one of the challenges of meeting current governmental (for example, Euro 6) NO_x regulations is the improvement of low temperature performance of the existing Cu-SSZ-13 based SCR catalysts. Additionally, light duty diesel (LDD) applications now require fast transient NO_x conversion response at low NH₃ storage levels. While current SCR technology has the maximum NO_x conversion at its highest NH₃ storage capacity, 2.2 g/L, light duty diesel customers demand the same maximum NO_x conversion from 0.5 g/L to 1 g/L NH₃ storage levels. Accordingly, an SCR catalyst is needed that shows optimal performance at significantly lower NH₃ filling level versus Cu-SSZ-13.

SUMMARY

[0008] A first aspect of the present invention is directed to a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component, wherein the catalyst is effective to catalyze the reduction of nitrogen oxides in the presence of a reductant.

[0009] In one or more embodiments, the 8-ring small pore molecular sieve is selected from the group consisting of AEI, AFT, AFX, CHA, EAB, ERI, KFI, LEV, SAS, SAT, and SAV. In a specific embodiment, the 8-ring small pore molecular sieve has the CHA crystal structure.

[0010] In one or more embodiments, the 8-ring small molecular sieve having the CHA-crystal structure is selected from the group consisting of aluminosilicate zeolite, a borosilicate, a gallosilicate, a SAPO, an ALPO, a MEAPSO and a MeAPO. In a specific embodiment, the 8-ring small pore molecular sieve having the CHA crystal structure is an aluminosilicate. In a more specific embodiment, the aluminosilicate is selected from

SSZ-13 and SSZ-62. In a specific embodiment, the aluminosilicate zeolite has a silica to alumina molar ratio in the range of 5 and 100.

[0011] In one or more embodiments, the 8-ring small pore molecular sieve having the CHA crystal structure is a SAPO.

[0012] In one or more embodiments, the molecular sieve is selected from the group consisting of SSZ-13, SSZ-62, natural chabazite, zeolite K-G, Linde D, Linde R, LZ-218, LZ-235, LZ-236, ZK-14, SAPO-34, SAPO-44, SAPO-47, and ZYT-6.

[0013] In one or more embodiments, the alkaline earth component is selected from barium, magnesium, beryllium, calcium, strontium, radium, and combinations thereof. In specific embodiments, the alkaline earth component is selected from barium, magnesium, calcium, and combinations thereof. In a very specific embodiment, the alkaline earth component is barium.

[0014] In one or more embodiments, the copper and alkaline earth component are exchanged into the 8-ring small pore molecular sieve.

[0015] In one or more embodiment, the catalyst exhibits higher NO_x conversion at 200°C than a catalyst comprising copper promoted aluminosilicate zeolite tested under similar conditions.

[0016] In one or more embodiments, the copper loading is in the range of 1 and 10% by weight, and the alkaline earth component loading is less than 5% by weight. In one or more embodiments, the copper loading is in the range of 2 and 8% by weight, and the alkaline earth component loading is less than 2.5% by weight. In a specific embodiment, the copper loading is in the range of 2 and 4% by weight, and the alkaline earth component loading is less than 1.5% by weight.

[0017] In one or more embodiments, the catalyst is effective to catalyze the selective catalytic reduction of nitrogen oxides in the presence of a reductant at temperatures between 200°C and 550°C without excessive generation or "make" of N₂O, a greenhouse gas.

[0018] A second aspect of the present invention is directed to a method for selectively reducing nitrogen oxides (NO_x), the method comprising contacting an exhaust gas stream containing NO_x with a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component.

[0019] In one or more embodiments, the 8-ring small pore molecular sieve is selected from the group consisting of AEI, AFT, AFX, CHA, EAB, ERI, KFI, LEV, SAS, SAT, and SAV. In one or more embodiments, the 8-ring small pore molecular sieve has the CHA crystal structure. The 8-ring small pore molecular sieve having the CHA crystal structure can be selected from the group consisting of aluminosilicate zeolite, SAPO, ALPO, and MeAPO. In one or more embodiments, the 8-ring small pore molecular sieve having the CHA crystal structure is selected from the group consisting of SSZ-13, SSZ-62, natural chabazite, zeolite K-G, Linde D, Linde R, LZ-218, LZ-235, LZ-236ZK-14, SAPO-34, SAPO-44, SAPO-47, ZYT-6, CuSAPO-34, CuSAPO-44, and CuSAPO-47.

[0020] In a specific embodiment, the 8-ring small pore molecular sieve having the CHA crystal structure is an aluminosilicate zeolite. The aluminosilicate zeolite can be selected from SSZ-13 and SSZ-62.

[0021] In one or more embodiments, the alkaline earth component is selected from barium, magnesium, calcium, and combinations thereof. In a specific embodiment, the alkaline earth component is barium.

[0022] Another aspect of the invention pertains to a catalytic article comprising the catalyst of described above in a washcoat deposited on a honeycomb substrate. The honeycomb substrate can comprise a wall flow filter substrate or a flow through substrate. Still another aspect pertains to an exhaust gas treatment system comprising the catalytic article described above disposed downstream from a diesel engine and an injector that adds a reductant to an exhaust gas stream from the engine.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] FIG. 1 compares NO_x conversion of a Cu-CHA sample (Example 1) with a Ba-Cu-CHA sample (Example 2).

[0024] FIG. 2 compares the NO_x conversion versus NH_3 storage for Cu-CHA (Example 1) and Ba-Cu-CHA samples (Example 2).

[0025] FIG. 3 represents an Infrared spectrum of Cu-CHA (Example 1) and Ba-Cu-CHA (Example 2) showing the N-O stretching vibrations after NO_x adsorption between 2000 and 1400 cm^{-1} .

[0026] FIG. 4 compares NO_x conversion, at 200 °C and 1 g/L NH₃ storage, of various alkaline earth metal promoted Cu-CHA.

[0027] FIG. 5 compares steady state NO_x conversion at 200 °C and 600 °C for various alkaline earth metal promoted Cu-CHA.

DETAILED DESCRIPTION

[0028] Before describing several exemplary embodiments of the invention, it is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

[0029] Governmental regulations mandate the use of NO_x reduction technologies for light and heavy-duty vehicles. Selective catalytic reduction (SCR) of NO_x using urea is an effective and dominant emission control technology for NO_x control. To meet governmental regulations, an SCR catalyst that has improved low and high temperature performance compared to the current Cu-SSZ-13 based benchmark technology is necessary. Provided is an SCR catalyst having NO_x conversion efficiency improvement at low NH₃ storage levels.

[0030] Embodiments of the invention are directed to catalysts including molecular sieves, methods for their preparation, catalytic articles, exhaust gas systems and methods for abating pollutants from exhaust gases using the catalysts.

[0031] With respect to the terms used in this disclosure, the following definitions are provided.

[0032] As used herein, molecular sieves refer to materials based on an extensive three-dimensional network of oxygen ions containing generally tetrahedral type sites and having a pore distribution. A zeolite is a specific example of a molecular sieve, further including silicon and aluminum. Reference to a "non-zeolite-support" or "non-zeolitic support" in a catalyst layer refers to a material that is not a molecular sieve or zeolite and that receives precious metals, stabilizers, promoters, binders, and the like through association, dispersion, impregnation, or other suitable methods. Examples of such non-zeolitic supports include, but are not limited to, high surface area refractory metal oxides. High surface area refractory metal oxide supports can comprise an activated compound

selected from the group consisting of alumina, zirconia, silica, titania, silica-alumina, zirconia-alumina, titania-alumina, lanthana-alumina, lanthana-zirconia-alumina, baria-alumina, baria-lanthana-alumina, baria-lanthana-neodymia-alumina, zirconia-silica, titania-silica, and zirconia-titania.

[0033] As used herein, the term "catalyst" refers to a material that promotes a reaction. As used herein, the phrase "catalyst composition" refers to a combination of two or more catalysts, for example a combination of two different materials that promote a reaction. The catalyst composition may be in the form of a washcoat. As used herein, the term "carrier" refers to a support that carries or supports a catalytic species such as a catalyzed honeycomb substrate.

[0034] As used herein, the term "substrate" refers to the monolithic material onto which the carrier is placed, typically in the form of a washcoat containing a plurality of carriers having catalytic species thereon. A washcoat is formed by preparing a slurry containing a specified solids content (e.g., 30-90% by weight) of carriers in a liquid vehicle, which is then coated onto a substrate and dried to provide a washcoat layer.

[0035] As used herein, the term "washcoat" has its usual meaning in the art of a thin, adherent coating of a catalytic or other material applied to a substrate carrier material, such as a honeycomb-type carrier member, which is sufficiently porous to permit the passage of the gas stream being treated.

[0036] In one or more embodiments, the substrate is a ceramic or metal having a honeycomb structure. Any suitable substrate may be employed, such as a monolithic substrate of the type having fine, parallel gas flow passages extending there through from an inlet or an outlet face of the substrate such that passages are open to fluid flow there through. The passages, which are essentially straight paths from their fluid inlet to their fluid outlet, are defined by walls on which the catalytic material is coated as a washcoat so that the gases flowing through the passages contact the catalytic material. The flow passages of the monolithic substrate are thin-walled channels, which can be of any suitable cross-sectional shape and size such as trapezoidal, rectangular, square, sinusoidal, hexagonal, oval, circular, etc. Such structures may contain from about 60 to about 900 or more gas inlet openings (i.e. cells) per square inch of cross section.

[0037] The ceramic substrate may be made of any suitable refractory material, e.g. cordierite, cordierite- α -alumina, silicon nitride, zircon mullite, spodumene, alumina-silica-magnesia, zircon silicate, sillimanite, a magnesium silicate, zircon, petalite, α -alumina, an aluminosilicate and the like.

[0038] The substrates useful for the catalyst carriers of embodiments of the present invention may also be metallic in nature and be composed of one or more metals or metal alloys. The metallic substrates may be employed in various shapes such as pellets, corrugated sheet or monolithic form. Specific examples of metallic substrates include the heat-resistant, base-metal alloys, especially those in which iron is a substantial or major component. Such alloys may contain one or more of nickel, chromium, and aluminum, and the total of these metals may advantageously comprise at least about 15 wt. % of the alloy, for instance, about 10 to 25 wt. % chromium, about 1 to 8 wt. % of aluminum, and about 0 to 20 wt. % of nickel.

[0039] "Rich gaseous streams" including rich exhaust streams mean gas streams that have a $\lambda < 1.0$.

[0040] "Rich periods" refer to periods of exhaust treatment where the exhaust gas composition is rich, i.e., has a $\lambda < 1.0$.

[0041] "Rare earth metal components" refer to one or more oxides of the lanthanum series defined in the Periodic Table of Elements, including lanthanum, cerium, praseodymium and neodymium. Rare earth metal components can include at least one rare earth metal selected from Ce, Pr, Nd, Eu, Nb, Sm, Yb, and La.

[0042] "Alkaline earth component" refers to one or more chemical elements defined in the Periodic Table of Elements, including beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).

[0043] One or more embodiments are directed to selective catalytic reduction catalysts. The catalysts comprise an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component. The catalyst is effective to catalyze the reduction of nitrogen oxides in the presence of a reductant. As used herein, "promoted" refers to a component that is intentionally added to the molecular sieve, as opposed to impurities inherent in the molecular sieve. Thus, a promoter is intentionally added to

enhance activity of a catalyst compared to a catalyst that does not have promoter intentionally added.

[0044] The molecular sieves have 8-ring pore openings and double-six ring secondary building units, for example, those having the following structure types: AEI, AFT, AFX, CHA, EAB, ERI, KFI, LEV, SAS, SAT, and SAV. According to one or more embodiments, it will be appreciated that by defining the molecular sieves by their structure type, it is intended to include the structure type and any and all isotopic framework materials such as SAPO, ALPO and MeAPO materials having the same structure type.

[0045] In more specific embodiments reference to an aluminosilicate zeolite structure type limits the material to molecular sieves that do not include phosphorus or other metals substituted in the framework. Of course, aluminosilicate zeolites may be subsequently ion-exchanged with one or more promoter metals such as iron, copper, cobalt, nickel, cerium or platinum group metals. However, to be clear, as used herein, "aluminosilicate zeolite" excludes aluminophosphate materials such as SAPO, ALPO, and MeAPO materials, and the broader term "zeolite" is intended to include aluminosilicates and aluminophosphates.

[0046] In general, the SCR catalyst based on an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component exhibits comparable NO_x conversion activity with Cu-SSZ-13 catalysts. In general, the catalyst exhibits both good low temperature NO_x conversion activity (NO_x conversion > 50% at 200°C) and good high temperature NO_x conversion activity (NO_x conversion > 70% at 450°C). The NO_x activity is measured under steady state conditions at maximum NH₃-slip conditions in a gas mixture of 500 ppm NO, 500 ppm NH₃, 10% O₂, 5% H₂O, balance N₂ at a volume-based space velocity of 80,000 h⁻¹.

[0047] As used herein, the term "Na⁺-form of chabazite" refers to the calcined form of this zeolite without any ion exchange. In this form, the zeolite generally contains a mixture of Na⁺ and H⁺ cations in the exchange sites. The fraction of sites occupied by Na⁺ cations varies depending on the specific zeolite batch and recipe.

[0048] A molecular sieve can be zeolitic--zeolites--or non-zeolitic, and zeolitic and non-zeolitic molecular sieves can have the chabazite crystal structure, which is also

referred to as the CHA structure by the International Zeolite Association. Zeolitic chabazite includes a naturally occurring tectosilicate mineral of a zeolite group with approximate formula: $(\text{Ca}, \text{Na}_2, \text{K}_2, \text{Mg})\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$ (e.g., hydrated calcium aluminum silicate). Three synthetic forms of zeolitic chabazite are described in "Zeolite Molecular Sieves," by D. W. Breck, published in 1973 by John Wiley & Sons, which is hereby incorporated by reference. The three synthetic forms reported by Breck are Zeolite K-G, described in J. Chem. Soc., p. 2822 (1956), Barrer et al; Zeolite D, described in British Patent No. 868,846 (1961); and Zeolite R, described in U.S. Patent No. 3,030,181, which are hereby incorporated by reference. Synthesis of another synthetic form of zeolitic chabazite, SSZ-13, is described in U.S. Pat. No. 4,544,538, which is hereby incorporated by reference. Synthesis of a synthetic form of a non-zeolitic molecular sieve having the chabazite crystal structure, silicoaluminophosphate 34 (SAPO-34), is described in U.S. Patent 4,440,871 and No. 7,264,789, which are hereby incorporated by reference. A method of making yet another synthetic non-zeolitic molecular sieve having chabazite structure, SAPO-44, is described in U.S. Patent No. 6,162,415, which is hereby incorporated by reference.

[0049] In one or more embodiments, the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component is selected from the group consisting of AEI, AFT, AFX, CHA, EAB, ERI, KFI, LEV, SAS, SAT, and SAV. In a specific embodiment, the 8-ring small pore molecular sieve can include all aluminosilicate, borosilicate, gallosilicate, MeAPSO, and MeAPO compositions. These include, but are not limited to SSZ-13, SSZ-62, natural chabazite, zeolite K-G, Linde D, Linde R, LZ-218, LZ-235, LZ-236, ZK-14, SAPO-34, SAPO-44, SAPO-47, ZYT-6, CuSAPO-34, CuSAPO-44, and CuSAPO-47. However, in specific embodiments, the 8-ring small pore molecular sieve will have the aluminosilicate composition, such as SSZ-13 and SSZ-62, which would exclude borosilicate, gallosilicate, MeAPSO, SAPO and MeAPO compositions.

[0050] In one or more embodiments, the 8-ring small pore molecular sieve has the CHA crystal structure and is selected from the group consisting of aluminosilicate zeolite having the CHA crystal structure, SAPO, ALPO, and MeAPO. In particular, the 8-ring small pore molecular sieve having the CHA crystal structure is an aluminosilicate

zeolite having the CHA crystal structure. In a specific embodiment, the 8-ring small pore molecular sieve having the CHA crystal structure will have an aluminosilicate composition, such as SSZ-13 and SSZ-62.

Wt% Copper:

[0051] The Cu content of the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component, calculated as CuO, in specific embodiments is at least about 1.5 wt.%, even more specifically at least about 2 wt.% and in even more specific embodiments at least about 2.5 wt.%, reported on a volatile-free basis. In even more specific embodiments, the Cu content of the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component, calculated as CuO, is in the range of up to about 10 wt.%, specifically up to about 9 wt.%, up to about 8 wt.%, up to about 7 wt.%, up to about 6 wt.%, up to about 5 wt.%, more specifically of up to about 4 wt.%, and even more specifically of up to about 3.5 wt.%, in each case based on the total weight of the calcined molecular sieve reported on a volatile free basis. Therefore, in specific embodiments, ranges of the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component, calculated as CuO, are from about 1 to about 10 wt.%, more specifically from about 1 to about 9 wt.%, and even more specifically from about 2 to about 8 wt.%, and even more specifically from about 2 to about 7 wt.%, in each case reported on a volatile-free basis. All wt.% values are reported on a volatile free basis.

Alkaline Earth Promoter

[0052] In one or more embodiments, the alkaline earth component is selected from barium, magnesium, beryllium, calcium, strontium, radium, and combinations thereof. In a specific embodiment, the alkaline earth component is selected from barium, magnesium, calcium, and combinations thereof. In a more specific embodiment, the alkaline earth component is barium.

[0053] In one or more embodiments, the alkaline earth component loading is less than 5% by weight. In a specific embodiment, the alkaline earth component loading is less than 4%, 3%, 2.5%, 2.0%, 1.5%, or 1% by weight. In a more specific embodiment, the alkaline earth component loading is less than 0.5% by weight.

[0054] In one or more embodiments, the copper and alkaline earth component are exchanged into the 8-ring small pore molecular sieve.

Silica/Alumina:

[0055] In specific embodiments, the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component is an aluminosilicate zeolite that has a mole ratio of silica to alumina greater than about 15, even more specifically greater than about 20. In specific embodiments, the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component has a mole ratio of silica to alumina in the range from about 20 to about 256, more specifically in the range from about 25 to about 40.

[0056] In specific embodiments, the atomic ratio of copper to aluminum exceeds about 0.25. In more specific embodiments, the ratio of copper to aluminum is from about 0.25 to about 1, even more specifically from about 0.25 to about 0.5. In even more specific embodiments, the ratio of copper to aluminum is from about 0.3 to about 0.4.

SCR Activity:

[0057] In specific embodiments, the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component exhibits an aged NO_x conversion at 200°C of at least 50% measured at a gas hourly space velocity of 80000 h⁻¹. In specific embodiments the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component exhibits an aged NO_x conversion at 450°C of at least 70% measured at a gas hourly space velocity of 80000 h⁻¹. More specifically the aged NO_x conversion at 200°C is at least 55% and at 450°C at least 75%, even more specifically the aged NO_x conversion at 200°C is at least 60% and at 450°C at least 80%, measured at a gas hourly volume-based space velocity of 80000 h⁻¹ under steady state conditions at maximum NH₃-slip conditions in a gas mixture of 500 ppm NO, 500 ppm NH₃, 10% O₂, 5% H₂O, balance N₂. The cores were hydrothermally aged in a tube furnace in a gas flow containing 10% H₂O, 10% O₂, balance N₂ at a space velocity of 4,000 h⁻¹ for 6h at 850°C.

[0058] The SCR activity measurement has been demonstrated in the literature, for example WO 2008/106519.

Sodium content:

[0059] In specific embodiments, the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component has a sodium content (reported as Na₂O on a volatile free basis) of below 2 wt.%, based on the total weight of the calcined molecular

sieve. In more specific embodiments, sodium content is below 1 wt.%, even more specifically below 2000 ppm, even more specifically below 1000 ppm, even more specifically below 500 ppm and most specifically below 100 ppm.

Na:Al:

[0060] In specific embodiments, the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component has an atomic sodium to aluminum ratio of less than 0.7. In more specific embodiments, the atomic sodium to aluminum ratio is less than 0.35, even more specifically less than 0.007, even more specifically less than 0.03 and even more specifically less than 0.02.

Na:Cu:

[0061] In specific embodiments, the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component has an atomic copper to sodium ratio of greater than 0.5. In more specific embodiments, the atomic copper to sodium ratio of greater than 1, even more specifically greater than 10, even more specifically greater than 50.

Conventional Zeolite Synthesis of CHA-type Molecular Sieves

[0062] In what may be referred to as a conventional synthesis of an molecular sieve having the CHA structure, a source of silica, a source of alumina, and a structure directing agent are mixed under alkaline aqueous conditions. Typical silica sources include various types of fumed silica, precipitated silica, and colloidal silica, as well as silicon alkoxides. Typical alumina sources include boehmites, pseudo-boehmites, aluminum hydroxides, aluminum salts such as aluminum sulfate or sodium aluminate, and aluminum alkoxides. Sodium hydroxide is typically added to the reaction mixture. A typical structure directing agent for this synthesis is adamantyltrimethyl ammonium hydroxide, although other amines and/or quaternary ammonium salts may be substituted or added to the latter directing agent. The reaction mixture is heated in a pressure vessel with stirring to yield the crystalline SSZ-13 product. Typical reaction temperatures are in the range of 100 and 200°C, and in specific embodiments between 135 and 170 °C. Typical reaction times are between 1 hr and 30 days, and in specific embodiments, between 10 hours and 3 days.

[0063] At the conclusion of the reaction, optionally the pH is adjusted to between 6 and 10, and in specific embodiments, between 7 and 7.5, and the product is filtered and washed with water. Any acid can be used for pH adjustment, and in specific embodiments nitric acid is used. Alternatively, the product may be centrifuged. Organic additives may be used to help with the handling and isolation of the solid product. Spray-drying is an optional step in the processing of the product. The solid product is thermally treated in air or nitrogen. Alternatively, each gas treatment can be applied in various sequences, or mixtures of gases can be applied. Typical calcination temperatures are in the 400°C to 850°C range.

Optionally NH₄-exchange to form NH₄-Chabazite:

[0064] Optionally, the obtained alkali metal zeolite is NH₄-exchanged to form NH₄-Chabazite. The NH₄⁻ ion exchange can be carried out according to various techniques known in the art, for example Bleken, F.; Bjorgen, M.; Palumbo, L.; Bordiga, S.; Svelle, S.; Lillerud, K.-P.; and Olsbye, U. *Topics in Catalysis* 52, (2009), 218-228.

Synthesis of CHA-Type Zeolites According to Embodiments of the Invention

[0065] According to one or more embodiments, methods for the synthesis of selective catalytic reduction catalysts comprising a copper-promoted 8-ring small pore molecular sieve also promoted with an alkaline earth. According to one or more embodiments, methods for the synthesis of selective catalytic reduction catalysts comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component are provided. Particularly, the catalyst comprises a SSZ-13 promoted with copper and barium. The synthesis of CHA-type zeolites promoted with copper and an alkaline earth, particularly CHA-type aluminosilicate zeolites such as SSZ-13 and SSZ-62 are provided.

[0066] Generally, barium is incorporated into a copper-promoted 8-ring small pore molecular sieve (e.g. Cu-SSZ-13) by dropwise addition of Ba²⁺ salt solution into an aqueous slurry of the copper-promoted 8-ring small pore molecular sieve. The pH is adjusted to about 5.5, followed by agitation of the mixture for at least 12 hours. The precursor slurry is pre-milled to desired D₉₀ value of particle size. The resultant barium

and copper promoted 8-ring small pore molecular sieve is then coated onto a ceramic flow-through honeycomb.

BET:

[0067] In specific embodiments, the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component exhibits a BET surface area, determined according to DIN 66131, of at least about 400 m²/g, more specifically of at least about 550 m²/g, even more specifically of at about 650 m²/g. In specific embodiments, the selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component exhibits a BET surface area in the range from about 400 to about 750 m²/g, more specifically from about 500 to about 750 m²/g, even more specifically from about 600 to mean length of crystallites:

[0068] In specific embodiments, the crystallites of the calcined 8-ring small pore molecular sieve promoted with copper and an alkaline earth component have a mean length in the range of from 10 nanometers to 100 micrometers, specifically in the range of from 50 nanometers to 5 micrometers, more specifically in the range of 50 nanometers to 500 nanometers as determined via SEM.

Shape:

[0069] The 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention may be provided in the form of a powder or a sprayed material obtained from above-described separation techniques, e.g. decantation, filtration, centrifugation, or spraying.

[0070] In general, the powder or sprayed material can be shaped without any other compounds, e.g. by suitable compacting, to obtain moldings of a desired geometry, e.g. tablets, cylinders, spheres, or the like.

[0071] By way of example, the powder or sprayed material is admixed with or coated by suitable modifiers well known in the art. By way of example, modifiers such as silica, alumina, zeolites or refractory binders (for example a zirconium precursor) may be used. The powder or the sprayed material, optionally after admixing or coating by suitable modifiers, may be formed into a slurry, for example with water, which is deposited upon a suitable refractory carrier (for example WO 2008/106519).

[0072] The 8-ring small pore molecular sieve promoted with copper and an alkaline earth component of embodiments of the invention may also be provided in the form of extrudates, pellets, tablets or particles of any other suitable shape, for use as a packed bed of particulate catalyst, or as shaped pieces such as plates, saddles, tubes, or the like.

[0073] In specific embodiments, the molecular sieve is substantially comprised of alumina and silica and has a silica to alumina ratio in the range of about 1 to 1000, and in specific embodiments from 1 to 500, and in more specific embodiments from 5 to 300, 5 to 200, 5 to 100, 10 to 90, 10 to 80, 10 to 70, 10 to 60, 10 to 50, 10 to 40, 10 to 35 and 10 to 30 are within the scope of the invention. In specific embodiments, the molecular sieve is SSZ-13 and/or SSZ-62 both promoted with copper and barium.

SCR / exhaust gas treatment system:

[0074] In general, the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component described above can be used as molecular sieve, adsorbent, catalyst, catalyst support or binder thereof. In especially specific embodiments, the material is used as catalyst.

[0075] Moreover, embodiments of the invention relates to a method of catalyzing a chemical reaction wherein the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention is employed as catalytically active material.

[0076] Among others, said catalyst may be employed as catalyst for the selective reduction (SCR) of nitrogen oxides (NO_x); for the oxidation of NH_3 , in particular for the oxidation of NH_3 slip in diesel systems; for the decomposition of N_2O ; for soot oxidation; for emission control in Advanced Emission Systems such as Homogeneous Charge Compression Ignition (HCCI) engines; as additive in fluid catalytic cracking (FCC) processes; as catalyst in organic conversion reactions; or as catalyst in "stationary source" processes. For applications in oxidation reactions, in specific embodiments an additional precious metal component is added to the copper chabazite (e.g. Pd, Pt).

[0077] Therefore, embodiments of the invention also relate to a method for selectively reducing nitrogen oxides (NO_x) by contacting a stream containing NO_x with a catalyst containing the 8-ring small pore molecular sieve promoted with copper and an

alkaline earth component according to embodiments of the invention under suitable reducing conditions; to a method of oxidizing NH_3 , in particular of oxidizing NH_3 slip in diesel systems, by contacting a stream containing NH_3 with a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention under suitable oxidizing conditions; to a method of decomposing of N_2O by contacting a stream containing N_2O with a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention under suitable decomposition conditions; to a method of controlling emissions in Advanced Emission Systems such as Homogeneous Charge Compression Ignition (HCCI) engines by contacting an emission stream with a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention under suitable conditions; to a fluid catalytic cracking FCC process wherein the selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component is employed as additive; to a method of converting an organic compound by contacting said compound with a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention under suitable conversion conditions; to a "stationary source" process wherein a catalyst is employed containing the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention.

[0078] In particular, the selective reduction of nitrogen oxides wherein the selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention is employed as catalytically active material is carried out in the presence of ammonia or urea. While ammonia is the reducing agent of choice for stationary power plants, urea is the reducing agent of choice for mobile SCR systems. Typically, the SCR system is integrated in the exhaust gas treatment system of a vehicle and, also typically, contains the following main components: selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline

earth component according to embodiments of the invention; a urea storage tank; a urea pump; a urea dosing system; a urea injector/nozzle; and a respective control unit.

Method of reducing NO_x :

[0079] Therefore, embodiments of the invention also relate to a method for selectively reducing nitrogen oxides (NO_x), wherein a gaseous stream containing nitrogen oxides (NO_x), for example exhaust gas formed in an industrial process or operation, and in specific embodiments also containing ammonia and/or urea, is contacted with the selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention.

[0080] The term nitrogen oxides, NO_x , as used in the context of embodiments of the invention designates the oxides of nitrogen, especially dinitrogen oxide (N_2O), nitrogen monoxide (NO), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), dinitrogen tetroxide (N_2O_4), dinitrogen pentoxide (N_2O_5), nitrogen peroxide (NO_3).

[0081] The nitrogen oxides which are reduced using a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention or an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component obtainable or obtained according to embodiments of the invention may be obtained by any process, e.g. as a waste gas stream. Among others, waste gas streams as obtained in processes for producing adipic acid, nitric acid, hydroxylamine derivatives, caprolactame, glyoxal, methyl-glyoxal, glyoxylic acid or in processes for burning nitrogenous materials may be mentioned.

[0082] In especially specific embodiments, a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention or the 8-ring small pore molecular sieve promoted with copper and an alkaline earth component obtainable or obtained according to embodiments of the invention is used for removal of nitrogen oxides (NO_x) from exhaust gases of internal combustion engines, in particular diesel engines, which operate at combustion conditions with air in excess of that required for stoichiometric combustion, i.e., lean.

[0083] Therefore, embodiments of the invention also relate to a method for removing nitrogen oxides (NO_x) from exhaust gases of internal combustion engines, in particular diesel engines, which operate at combustion conditions with air in excess of that required for stoichiometric combustion, i.e., at lean conditions, wherein a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component according to embodiments of the invention or an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component obtainable or obtained according to embodiments of the invention is employed as catalytically active material.

Exhaust gas treatment system:

[0084] Embodiments of the invention relate to an exhaust gas treatment system comprising an exhaust gas stream optionally containing a reductant like ammonia, urea and/or hydrocarbon, and in specific embodiments, ammonia and/or urea, and a selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component, obtainable or obtained by above-described process, disposed on a substrate, for example, a soot filter and a diesel oxidation catalyst.

[0085] The soot filter, catalyzed or non-catalyzed, may be upstream or downstream of said catalytic article. The diesel oxidation catalyst in specific embodiments is located upstream of said catalytic article. In specific embodiments, said diesel oxidation catalyst and said catalyzed soot filter are upstream from said catalytic article.

[0086] In specific embodiments, the exhaust is conveyed from the diesel engine to a position downstream in the exhaust system, and in more specific embodiments, containing NO_x, where a reductant is added and the exhaust stream with the added reductant is conveyed to said catalytic article.

[0087] For example, a catalyzed soot filter, a diesel oxidation catalyst and a reductant are described in WO 2008/106519 which is incorporated by reference. In specific embodiments, the soot filter comprises a wall-flow filter substrate, where the channels are alternately blocked, allowing a gaseous stream entering the channels from one direction (inlet direction), to flow through the channel walls and exit from the channels from the other direction (outlet direction).

[0088] An ammonia oxidation catalyst may be provided downstream of the catalytic article to remove any slipped ammonia from the system. In specific embodiments, the AMOX catalyst may comprise a platinum group metal such as platinum, palladium, rhodium or combinations thereof. In more specific embodiment, the AMOX catalyst can include a washcoat containing an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component.

[0089] Such AMOX catalysts are useful in exhaust gas treatment systems including an SCR catalyst. As discussed in commonly assigned United States Patent No. 5,516,497, the entire content of which is incorporated herein by reference, a gaseous stream containing oxygen, nitrogen oxides and ammonia can be sequentially passed through first and second catalysts, the first catalyst favoring reduction of nitrogen oxides and the second catalyst favoring the oxidation or other decomposition of excess ammonia. As described in United States Patent No. 5,516,497, the first catalysts can be a SCR catalyst comprising a zeolite and the second catalyst can be an AMOX catalyst comprising a zeolite.

[0090] AMOX and/or SCR catalyst composition can be coated on the flow through or wall-flow filter. If a wall flow substrate is utilized, the resulting system will be able to remove particulate matter along with gaseous pollutants. The wall-flow filter substrate can be made from materials commonly known in the art, such as cordierite, aluminum titanate or silicon carbide. It will be understood that the loading of the catalytic composition on a wall flow substrate will depend on substrate properties such as porosity and wall thickness, and typically will be lower than loading on a flow through substrate.

Ion Exchange of Metal

[0091] In order to promote the SCR of oxides of nitrogen, a suitable metal is exchanged into the molecular sieve material. Suitable metals include, but are not limited to copper, iron, cobalt, nickel, cerium, platinum, palladium, rhodium and combinations thereof. In specific embodiments, copper is ion exchanged into the molecular sieve. The metal can be exchanged after manufacture of the molecular sieve. According to one or more embodiments, at least a portion of the metal can be included in the tailored colloid

such that the tailored colloid contains the structure directing agent, a silica source, and alumina source and a metal ion (e.g., copper) source.

[0092] For additional promotion of the SCR of oxides of nitrogen, a suitable alkaline earth is exchanged into the molecular sieve material. Suitable alkaline earths include, but are not limited to, barium, magnesium, beryllium, calcium, strontium, radium, and combinations thereof. In specific embodiments, the alkaline earth component is selected from barium, magnesium, calcium, and combinations thereof. In very specific embodiments, barium is exchanged into the molecular sieve. The metal can be exchanged after manufacture of the molecular sieve.

Copper-exchange into to alkali metal or NH_4 -Chabazite to form metal-Chabazite:

[0093] In specific embodiments, copper is ion exchanged into alkali metal or NH_4 -Chabazite to form Cu-Chabazite. When copper acetate is used, the copper concentration of the liquid copper solution used in the copper ion-exchange is in specific embodiments in the range from about 0.01 to about 0.4 molar, more specifically in the range from about 0.05 to about 0.3 molar, even more specifically in the range from about 0.1 to about 0.25 molar, even more specifically in the range from about 0.125 to about 0.25 molar, even more specifically in the range from about 0.15 to about 0.225 molar and even more specifically in the range from about 0.2.

[0094] According to an embodiment of the present invention, the 8-ring small pore molecular sieve of the invention is used in a catalytic process, for example, as a catalyst and/or catalyst support, and more specifically as a catalyst. In general, the 8-ring small pore molecular sieve of the invention can be used as a catalyst and/or catalyst support in any conceivable catalytic process, wherein processes involving the conversion of at least one organic compound, more specifically of organic compounds comprising at least one carbon - carbon and/or carbon - oxygen and/or carbon - nitrogen bond, more specifically of organic compounds comprising at least one carbon - carbon and/or carbon - oxygen bond, and even more specifically of organic compounds comprising at least one carbon - carbon bond. In particularly specific embodiments of the present invention, the 8-ring small pore molecular sieve is used as a catalyst and/or catalyst support in any one or more of methanol-to-olefin (MTO) reactions, ethylene-to-propylene (ETP) reactions,

as well as of the co-reaction of methanol and ethylene (CME). The processes involve contacting the compounds with the catalysts according to embodiments of the invention.

[0095] According to a further embodiment of the present invention, the 8-ring small pore molecular sieve of the invention used in a catalytic process involving the conversion of at least one compound comprising at least one nitrogen - oxygen bond. According to one or more embodiments of the present invention the 8-ring small pore molecular sieve is used as a catalyst and/or catalyst support in a selective catalytic reduction (SCR) process for the selective reduction of nitrogen oxides NO_x ; for the oxidation of NH_3 , in particular for the oxidation of NH_3 slip in diesel systems; for the decomposition of N_2O . The term nitrogen oxides, NO_x , as used in the context of the present invention designates the oxides of nitrogen, especially dinitrogen oxide (N_2O), nitrogen monoxide (NO), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), dinitrogen tetroxide (N_2O_4), dinitrogen pentoxide (N_2O_5), nitrogen peroxide (NO_3). According to particularly specific embodiments of the present invention, the 8-ring small pore molecular sieve used in a catalytic process involving the conversion of at least one compound comprising at least one nitrogen-oxygen bond comprises Cu. The process can be accomplished by contacting the compound with a catalyst according to an embodiment of the invention.

[0096] Therefore, the present invention also relates to a method for selectively reducing nitrogen oxides NO_x by contacting a stream containing NO_x with a catalyst containing the 8-ring small pore molecular sieve according to the present invention under suitable reducing conditions; to a method of oxidizing NH_3 , in particular of oxidizing NH_3 slip in diesel systems, by contacting a stream containing NH_3 with a catalyst containing the 8-ring small pore molecular sieve according to the present invention under suitable oxidizing conditions; to a method of decomposing of N_2O by contacting a stream containing N_2O with a catalyst containing the 8-ring small pore molecular sieve under suitable decomposition conditions; to a method of controlling emissions in Advanced Emission Systems such as Homogeneous Charge Compression Ignition (HCCI) engines by contacting an emission stream with a catalyst containing the 8-ring small pore molecular sieve under suitable conditions; to a fluid catalytic cracking FCC process wherein the 8-ring small pore molecular sieve is employed as additive; to a method of

converting an organic compound by contacting said compound with a catalyst containing the 8-ring small pore molecular sieve under suitable conversion conditions; to a "stationary source" process wherein a catalyst is employed containing the molecular sieve material.

[0097] Accordingly, embodiments of the present invention also relate to a method for selectively reducing nitrogen oxides NO_x , wherein a gaseous stream containing nitrogen oxides NO_x , specifically also containing ammonia and/urea, is contacted with the 8-ring small pore molecular sieve according to the present invention or the 8-ring small pore molecular sieve material obtainable or obtained according to the present invention, for example, in the form of a molded catalyst, specifically as a molded catalyst wherein the 8-ring small pore molecular sieve is deposited on a suitable refractory carrier, still more specifically on a "honeycomb" carrier.

[0098] The nitrogen oxides which are reduced using a catalyst containing the 8-ring small pore molecular sieve obtainable or obtained according to embodiments of the present invention may be obtained by any process, e.g. as a waste gas stream. Among others, waste gas streams as obtained in processes for producing adipic acid, nitric acid, hydroxylamine derivatives, caprolactame, glyoxal, methyl-glyoxal, glyoxylic acid or in processes for burning nitrogenous materials may be mentioned.

[0099] In specific embodiments, the 8-ring small pore molecular sieve or the 8-ring small pore molecular sieve obtainable or obtained according to embodiments of the present invention is used as a molded catalyst, still more specifically as a molded catalyst wherein the 8-ring small pore molecular sieve is deposited on a suitable refractory carrier, still more specifically on a "honeycomb" carrier, for the selective reduction of nitrogen oxides NO_x , i.e. for selective catalytic reduction of nitrogen oxides. In particular, the selective reduction of nitrogen oxides wherein the 8-ring small pore molecular sieve according to an embodiment of the present invention is employed as catalytically active material is carried out in the presence ammonia or urea. While ammonia is the reducing agent of choice for stationary power plants, urea is the reducing agent of choice for mobile SCR systems. Typically, the SCR system is integrated in the engine and vehicle design and, also typically, contains the following main components: SCR catalyst containing the 8-ring small pore molecular sieve according to an embodiment of the

present invention; a urea storage tank; a urea pump; a urea dosing system; a urea injector/nozzle; and a respective control unit.

[00100] More specific embodiments pertain to the use of a catalyst containing the 8-ring small pore molecular sieve according to the present invention or the 8-ring small pore molecular sieve obtainable or obtained according to the inventive process for removal of nitrogen oxides NO_x from exhaust gases of internal combustion engines, in particular diesel engines, which operate at combustion conditions with air in excess of that required for stoichiometric combustion, i.e. in a lean operation mode.

[00101] Therefore, embodiments the present invention also relates to a method for removing nitrogen oxides NO_x from exhaust gases of internal combustion engines, in particular diesel engines, which operate at combustion conditions with air in excess of that required for stoichiometric combustion, i.e., at lean conditions, wherein a catalyst containing the 8-ring small pore molecular sieve according to the present invention or the 8-ring small pore molecular sieve obtainable or obtained according to the present invention is employed as catalytically active material.

[00102] Embodiments of the present invention therefore relates to the use of the 8-ring small pore molecular sieve of the invention, in particular in the field of catalysis and/or in the treatment of exhaust gas, wherein said exhaust gas treatment comprises industrial and automotive exhaust gas treatment. In these and other applications, the 8-ring small pore molecular sieve of the present invention can by way of example be used as a molecular sieve, catalyst, and/or catalyst support.

[00103] The invention is now described with reference to the following examples. Before describing several exemplary embodiments of the invention, it is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

EXAMPLES

[00104] EXAMPLE 1-PREPARATION OF CATALYST SAMPLES (Cu-SSZ-13, Comparative Example)

[00105] A Cu-CHA powder catalyst was prepared by mixing 100 g of NH_4^+ -form CHA, having a silica/alumina mole ratio of 30, with 400 mL of a copper(II) acetate solution of 1.0 M. An ion-exchange reaction between the NH_4^+ -form CHA and the copper ions was carried out by agitating the slurry at 80° C for 1 hour. The resulting mixture was then filtered, washed with 800 mL of deionized water in three portions until the filtrate was clear and colorless, which indicated that substantially no soluble or free copper remained in the sample, and the washed sample was dried in air at room temperature.

[00106] The resulting Cu-CHA product was then calcined at 640° C in air for 6 hours. The obtained Cu-CHA catalyst comprised CuO at 2 to 3.5% by weight, as determined by ICP analysis. A Cu-CHA slurry was prepared by mixing 90 g of Cu-CHA, as described above, with 215 mL of deionized water. The slurry was milled and a binder of zirconium acetate in dilute acetic acid (containing 30% ZrO_2) was added into the slurry with agitation.

The slurry was coated onto 1"Dx3"L cellular ceramic cores, having a cell density of 400 cpsi (cells per square inch) and a wall thickness of 6 mil. The coated cores were dried at 110° C for 3 hours and calcined at 450° C for 1 hour. The coating process was repeated once to obtain a target washcoat loading of 2 to 3 g/in³.

EXAMPLE 2

[0001] Barium incorporated Cu-SSZ-13 (Ba-Cu-SSZ-13) is prepared by drop-wise addition of Ba^{2+} salt solution into an aqueous slurry of Cu-SSZ-13 prepared in accordance with Example 1. The Cu-CHA filter cake obtained in Example 1 was crushed and then calcined at 600°C for 4 hours. An aqueous slurry was then prepared to 45% target solids, followed by addition of 5% ZrOAc binder, based on the zeolite solids. The mixture was mixed well, and then was milled. A solution of $\text{Ba}(\text{OAc})_2$ (30 mL, 0.00822 g per gram of zeolite for 0.5wt% BaO loading) was added dropwise to the aqueous slurry with stirring. The pH was adjusted to 4.5 using 15% ammonium hydroxide solution. The slurry was rolled overnight (for at least 12 hours) for in-situ ion exchange of Ba^{2+} . The resultant Ba-Cu-SSZ-13 slurry is coated onto ceramic flow-through honeycombs.

[00107]

EXAMPLE 3-SAMPLE TESTING

[00108] For the preparation of coated monolithic test scores, the filtercake (water content of 45 % measured after calcination at 600°C in air for 1 hour) was made into a slurry of 38-45% solid content by adding deionized water. The Cu-CHA slurry was then milled in a ceramic ball mill to a particle size of D_{90} of less than 10 μm (for example 4 to 10 μm) measured with a Sympatec particle size analyzer using forward Laser scattering. No acid or binder was added to the slurry in order to probe the intrinsic activity of the catalyst. The milled slurry was coated onto a ceramic monolith (NGK) of 1" diameter and 2" length having 400 cpsi cell density and 6 mil wall thickness. The target dry gain was 2.3 g/in^3 which corresponds to the loading of active catalyst in WO 2008/106519. Typically two to three coats were needed to reach that target, the solid content of the additional coats has been adjusted to meet the desired target dry gain increase. After each coat the core was dried for 3h at 90°C in air. The last drying step was followed by a calcination for 1h at 450°C in air in a muffle funnel.

[00109] Nitrogen oxides selective catalytic reduction (SCR) efficiency and selectivity of a fresh catalyst core was measured by adding a feed gas mixture of 500 ppm of NO, 500 ppm of NH_3 , 10% O_2 , 5% H_2O , balanced with N_2 to a steady state reactor containing a 1"D x 3"L catalyst core. The reaction was carried at a space velocity of 80,000 hr^{-1} across a 150° C to 460° C temperature range.

[00110] Samples were hydrothermally aged in the presence of 10% H_2O at 750° C for 5 hours, followed by measurement of the nitrogen oxides SCR efficiency and selectivity by the same process as outlined above for the SCR evaluation on a fresh catalyst core.

[00111] Figure 1 compares Example 1 with Example 2 for steady state NO_x conversion obtained on a lab reactor. The results are summarized in Table 1.

Table 1:

EXAMPLE #	TEMPERATURE (°C)	NO_x CONVERSION (%)
1	200	54
	250	91
	300	96

	450	87
	550	80
2	200	70
	250	93
	300	95
	450	86
	550	78

[00112] Figure 2 compares the NO_x conversion versus NH₃ storage for Example 1 and Example 2 obtained on a lab reactor at 190 °C.

[00113] The results are summarized in Table 2.

Table 2:

EXAMPLE #	NO _x CONVERSION (%)	NH ₃ STORAGE @ 190°C (g/L)
1	21	0.5
	32	1.0
	40	1.5
	45	2.0
2	24	0.5
	39	1.0
	50	1.5
	60	2.0

[00114] The aged Ba-Cu-SSZ-13 has 10% higher absolute NO_x conversion compared to Cu-SSZ-13 at 200°C. This improvement of low temperature SCR performance occurs at lower NH₃ storage values compared to that of Cu-SSZ-13. Among different Ba loading studied (0.5, 1, and 5 wt% BaO), the 0.5 wt% Ba sample showed the highest performance improvement, and the 5 wt% Ba loading showed detrimental effects on SCR performance.

[00115] EXAMPLE 4 – NO_x Drift

[00116] NO_x adsorption was measured on 2:1 DE Cu(CHA) to Liquid Exchange FeCHA samples to determine the effect of BaO. NO_x DRIFT experiments were performed on the Excalibur FT-IR instrument. Samples were dehydrated at 450°C for 1 hour in dry nitrogen(g) and argon(g). The samples were then cooled to room temperature, and adsorbed with 1% NO_x in argon(g). Spectra were collected after 45 minutes of desorption. N-O stretching vibrations are shown in an IR spectral comparison (Figure 3) after NO_x adsorption between 2000 and 1400 cm⁻¹.

[00117] The results show that with the addition of BaO, a much higher concentration of NO_x is stored on the catalyst surface.

[00118] EXAMPLE 5- Additional Metal Promoters

Additional metals, Ca, Mg and Sr were incorporated into Cu-CHA to produce Ca-Cu-CHA, Mg-Cu-CHA, and Sr-Cu-CHA; similar to the procedures in Example 2 in an amount of 0.5 wt. %. Figure 4 shows NO_x conversion of each sample at 200 °C at 1 g/L NH₃ storage. Ba-Cu-CHA, Ca-Cu-CHA, and Sr-Cu-CHA showed improved low temperature conversion at 1 g/L NH₃ storage compared to Cu-CHA. Figure 5 compares the steady state NO_x conversion at 200 °C and 600 °C for Example 1, Example 2, and other (Ca, Sr) alkaline earth elements promoted in Cu-CHA. Example 2, Ca-Cu-CHA, and Sr-Cu-CHA show SCR performance improvement vs. Example 1 at 200 °C. Example 2 and Sr-Cu-CHA show SCR performance improvement vs. Example 1 at 600 °C.

[00119] Reference throughout this specification to “one embodiment,” “certain embodiments,” “one or more embodiments” or “an embodiment” means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the invention. Thus, the appearances of the phrases such as “in one or more embodiments,” “in certain embodiments,” “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily referring to the same embodiment of the invention. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

[00120] Although the invention herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present invention. It will be apparent to those skilled in the art that various modifications and variations can be made to the method and apparatus of the present invention without departing from the spirit and scope of the invention. Thus, it is intended that the present invention include modifications and variations that are within the scope of the appended claims and their equivalents.

What is claimed is:

1. A selective catalytic reduction catalyst comprising an 8-ring small pore molecular sieve promoted with copper and an alkaline earth component, wherein the catalyst is effective to catalyze the reduction of nitrogen oxides in the presence of a reductant.
2. The catalyst of claim 1, wherein the 8-ring small pore molecular sieve is selected from the group consisting of AEI, AFT, AFX, CHA, EAB, ERI, KFI, LEV, SAS, SAT, and SAV.
3. The catalyst of claim 2, wherein the 8-ring small pore molecular sieve has the CHA crystal structure.
4. The catalyst of claim 3, wherein the 8-ring small pore molecular sieve having the CHA crystal structure is selected from the group consisting of aluminosilicate zeolite, a borosilicate, a gallosilicate, a SAPO, an ALPO, a MEAPSO and a MeAPO.
5. The catalyst of claim 4, wherein the molecular sieve is selected from the group consisting of SSZ-13, SSZ-62, natural chabazite, zeolite K-G, Linde D, Linde R, LZ-218, LZ-235, LZ-236, ZK-14, SAPO-34, SAPO-44, SAPO-47, and ZYT-6.
6. The catalyst of claim 3, wherein the 8-ring small pore molecular sieve having the CHA crystal structure is an aluminosilicate zeolite.
7. The catalyst of claim 5, wherein the aluminosilicate zeolite is selected from SSZ-13 and SSZ-62.
8. The catalyst of claim 3, wherein the 8-ring small pore molecular sieve having the CHA crystal structure is a SAPO.

9. The catalyst of claim 1, wherein the alkaline earth component is selected from barium, magnesium, calcium, strontium, and combinations thereof.

10. The catalyst of claim 9, wherein the alkaline earth component is selected from barium, magnesium, calcium, and combinations thereof.

Figure 1

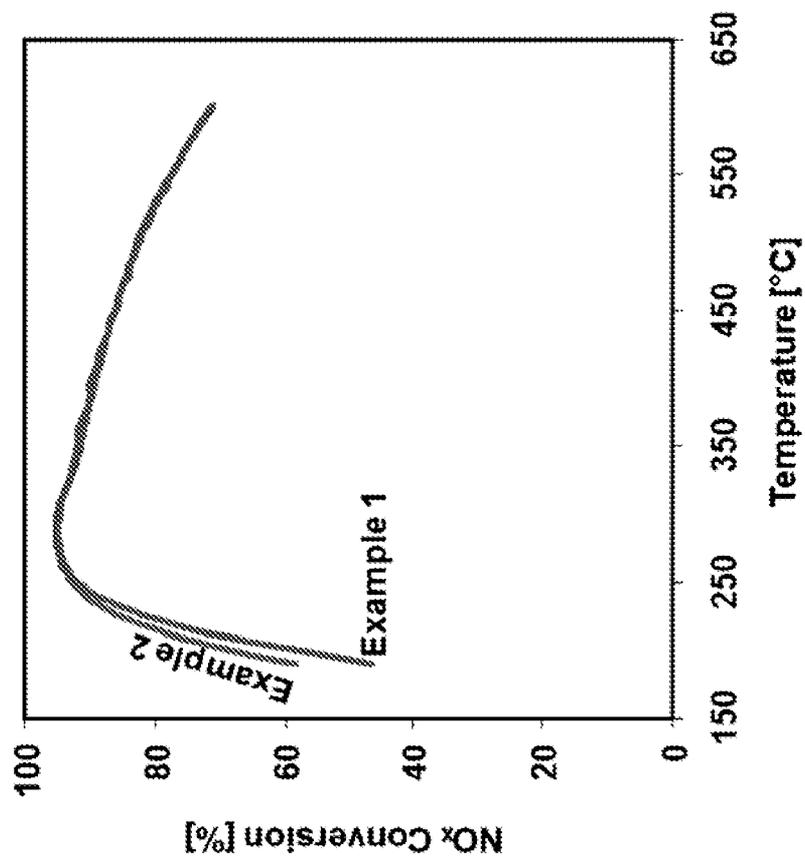


Figure 2

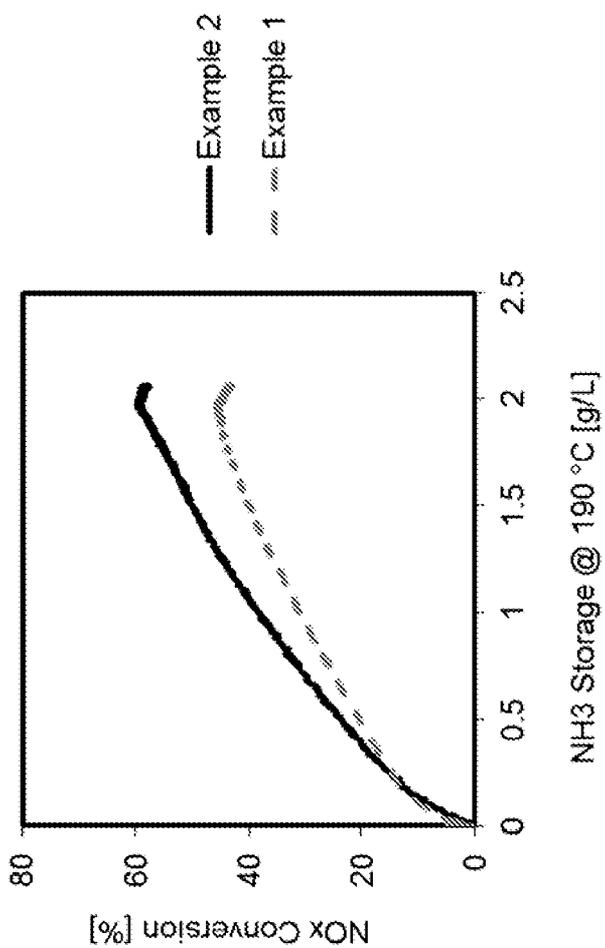


Figure 3

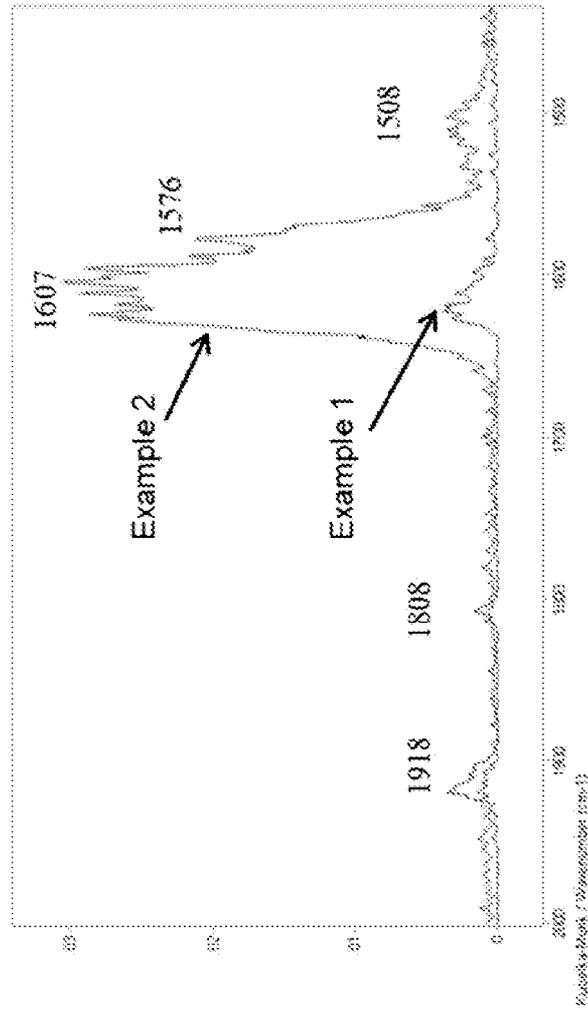


Figure 4

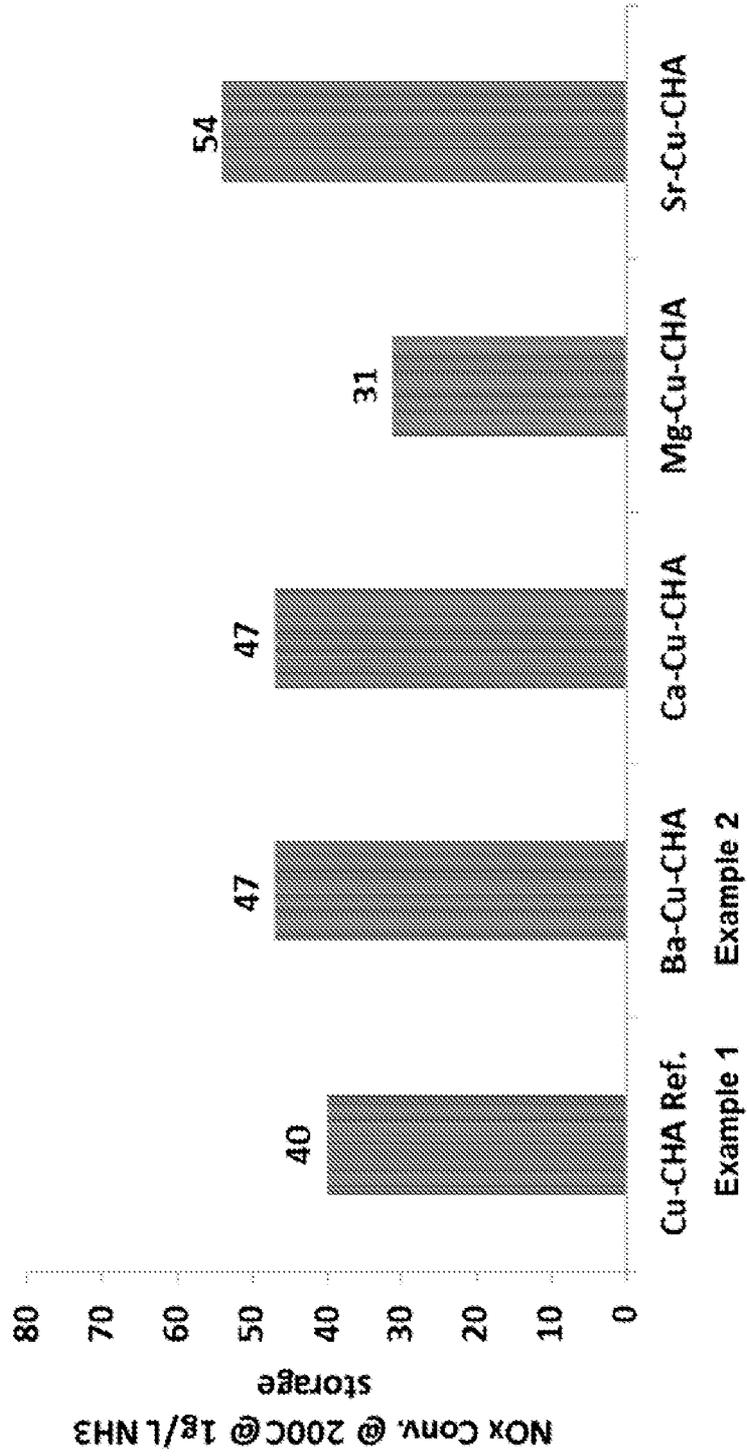
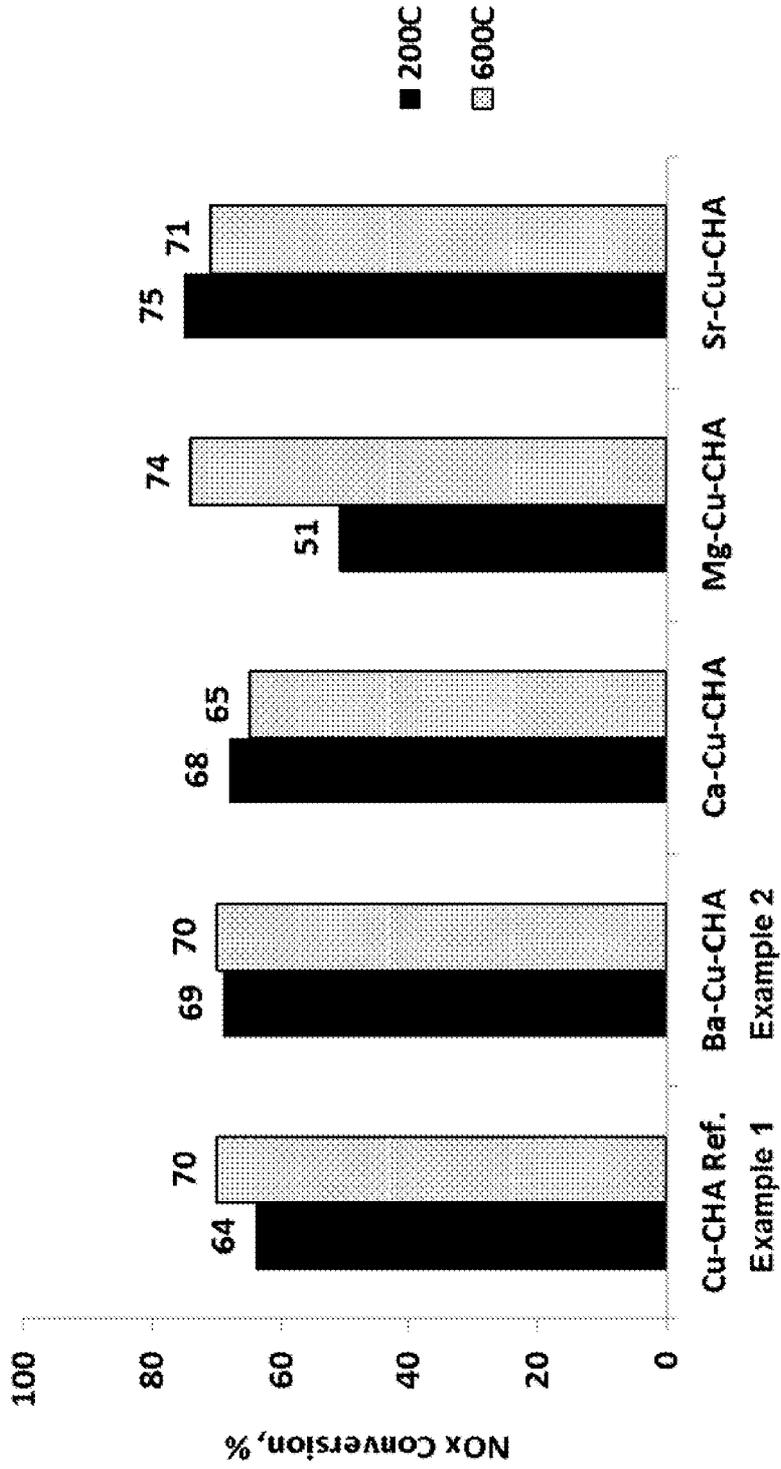


Figure 5



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/065501**A. CLASSIFICATION OF SUBJECT MATTER****B01J 23/72(2006.01)i, B01J 23/02(2006.01)i, B01J 29/06(2006.01)i**

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

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
B01J 23/72; B01J 23/02; B01J 29/06Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: selective catalytic reduction, catalyst, 8-ring small pore molecular sieve, copper, alkaline earth, nitrogen oxide, reduction, CHA, SAPO, ALP**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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Y	US 8101147 B2 (ANDERSEN, PAUL JOSEPH et al.) 24 January 2012 See abstract; claims 1-11.	1-10
Y	TERAOKA, YASUTAKE et al., "Influence of cocations on catalytic activity of copper ion-exchanged ZSM-5 zeolite for reduction of nitric oxide with ethene in the presence of oxygen", Catalysis Letters, 1992, Vol. 12, pages 361-366. See abstract.	1-10
A	ISHIHARA, TATSUMI et al., "Copper Ion-Exchanged SAPO-34 as a Thermostable Catalyst for Selective Reduction of NO with C3H6", Journal of Catalysis, 1997, Vol. 169, pages 93-102. See abstract.	1-10
A	US 7601662 B2 (BULL, IVOR et al.) 13 October 2009 See abstract; claims 1-38.	1-10
A	US 7435855 B2 (BOSCH, MARCO et al.) 14 October 2008 See abstract; claims 1-28.	1-10

 Further documents are listed in the continuation of Box C. See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

26 December 2013 (26.12.2013)

Date of mailing of the international search report

27 December 2013 (27.12.2013)

Name and mailing address of the ISA/KR

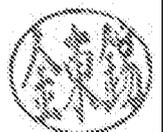

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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