

(21) Application No: **1602702.1**
(22) Date of Filing: **16.02.2016**
(30) Priority Data:
(31) **62118837** (32) **20.02.2015** (33) **US**

(51) INT CL:
B01J 29/76 (2006.01) **B01J 29/56** (2006.01)
B01J 29/90 (2006.01) **B01J 35/00** (2006.01)
B01J 37/02 (2006.01)

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**Donny Gasah Synthesis and characterization of Cu/
Ni-Zeolite-A for the direct conversion of methane to
liquid hydrocarbon, Faculty of chemical and natural
resources engineer, Universiti Malaysia Pahang,
published May 2008**

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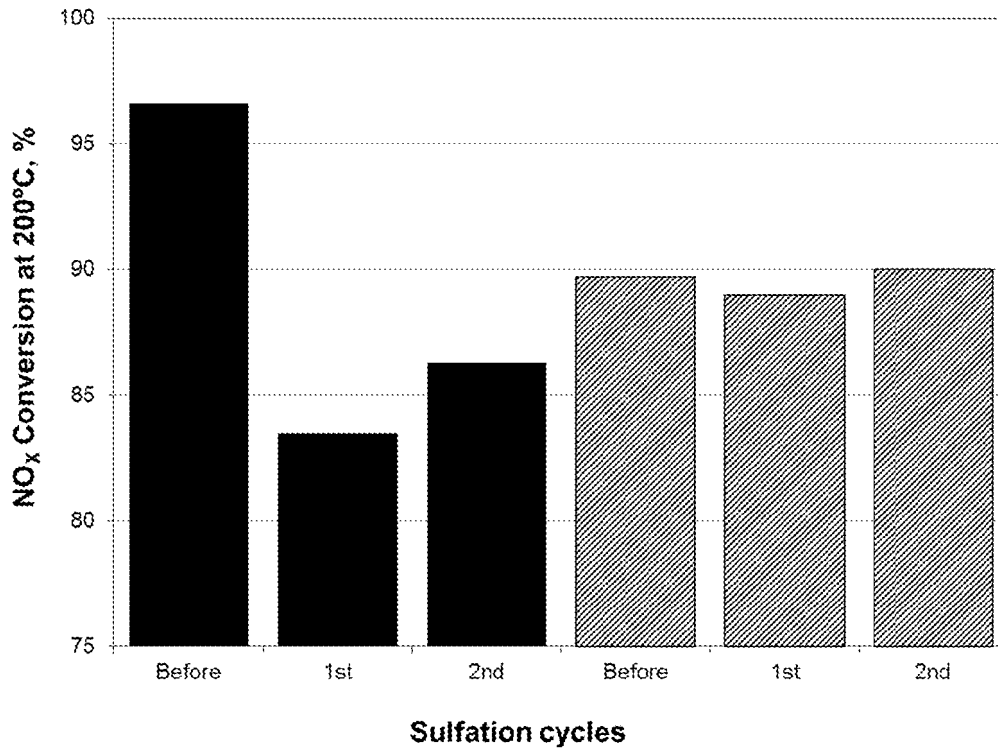
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(58) Field of Search:
INT CL **B01J**
Other: **WPI, EPODOC**

(54) Title of the Invention: **Bi-metal molecular sieve catalysts**
Abstract Title: **Bi-metal molecular sieve catalysts**

(57) Catalyst composition comprising a small pore molecular sieve, 0.5-5 weight percent of copper and/or iron (Tm), based on total molecular sieve weight, and 0.5-5 wt% nickel, wherein the Tm:Ni ratio is between 10:1 and 1:2. The nickel and copper/iron may be incorporated in to the sieve during synthesis and a majority of them may be present as extra-framework metals. The sieve may have a CHA or AEI framework, and may be a zeolite having a silica to alumina ratio of 10:50. The framework may be essentially free of non-aluminium metals. Included is a method of synthesis a molecular sieve comprising heating an admixture of sources of silica, alumina, copper and/or iron, nickel, at least one structure directing agent and optionally a phosphate to form zeolites and then separating the sieves from the mother liquor. Claims are also present for a catalytic article comprising a substrate coated with the composition, a method and system for treating exhaust gas using the composition and a method for regenerating a catalyst.

FIGURE 1



BI-METAL MOLECULAR SIEVE CATALYSTS

BACKGROUND

Field of Invention:

5 The present invention relates to method for synthesizing a molecular sieve containing metals and to the use of such molecular sieves as catalysts for treating combustion exhaust gas.

Description of Related Art:

10 Small pore molecular sieves, such as zeolites and silicoaluminophosphates (SAPOs), with Cu^{2+} cations in extra-framework positions show excellent activity in the selective catalytic reduction (SCR) of NO with NH_3 , an important conversion for the abatement of pollution from lean burn engines. Materials with the CHA and AEI topology types (zeolites SSZ-13 and SSZ-39 and SAPOs-34 and -18, respectively) have been studied for this reaction. Cu^{2+} cations can be introduced into the solids by cation exchange of materials from which the original alkylammonium structure directing agents have been removed by calcination. Apart from requiring a separate preparative step, in SAPOs this can also lead to a reduction in crystallinity and an inhomogeneous distribution of Cu^{2+} cations.

15 However, copper is easily poisoned and/or deactivated by small amounts of sulfur which are often present in exhaust gases resulting from hydrocarbon combustion, particularly diesel exhaust gas. Accordingly, there remains a need for sulfur tolerate SCR catalysts. This invention satisfies that need amongst others.

SUMMARY OF THE INVENTION

25 Applicants have discovered that a bi-metal molecular sieve catalyst promoted with nickel in combination with another metal such as iron and/or copper unexpectedly improves the catalyst's resistance to sulfur poisoning and deactivation while simultaneously achieving a consistently high level of NO_x conversion at low temperatures. Due to nickel's strong affinity for sulfur, particularly in lean (i.e., oxygen abundant) exhaust gases, it is surprising and unexpected to find that nickel can be beneficially used in a high sulfur environment or as a means of mitigating sulfur poisoning. Moreover, nickel promoted catalysts generally have poor NO_x conversion performance at low temperatures. The consistently high NO_x conversion performance of the present nickel-containing small pore molecular sieve catalyst is, therefore, also surprising.

Applicants have also discovered a novel synthesis route to incorporating both nickel and copper into a small pore molecular sieve. Typically, post synthesis exchange of two transition metals into a molecular sieve results in many complications. If co-impregnation of both metals is used, either through ion exchange or incipient wetness, metal solubilities often lead to a lack of uniformity of the two metals throughout the molecular sieve crystals. For sequential exchange, the competition between metals to exchange can often lead to one metal blocking access to exchange sites from the other metal. The inventors have found that incorporating both metals during molecular sieve synthesis can be achieved without destabilizing the molecular sieve during formation.

Accordingly, provided is a catalyst composition comprising a small pore molecular sieve, about 0.5 - 5 weight percent of a transition metal (T_M) selected from copper and/or iron (based on the total weight of the molecular sieve), and about 0.5 - 5 weight percent nickel (based on the total weight of the molecular sieve), wherein the transition metal and nickel are present in a T_M :Ni ratio of about 10:1 to about 1:2. Also provided is a SCR catalyst containing such a Ni/ T_M /molecular sieve, wherein the catalyst is effective for reducing NO_x to N_2 in the presence of a reductant. Also provided is a catalyst article comprising a honeycomb substrate coated or extruded with such an SCR catalyst. Also provided is an exhaust gas treatment system comprising such a catalyst article and an upstream ammonia or ammonia precursor injector, a HC injector, or a NO_x absorber catalyst.

Also provided is a method for synthesizing a bi-metal zeolite comprising the steps of (1) heating an admixture comprising a source of silica, a source of alumina, a source of copper and/or iron, a source of nickel, and at least one structure directing agent to form molecular sieve crystals containing nickel and at least one of copper and iron, and (2) separating the molecular sieve crystals from the mother liquor.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is graphical depiction of comparative data showing the NO_x conversion performance of the catalyst of present invention relative to a conventional catalyst.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The invention, at least in part, is directed to a catalyst and method for improving environmental air quality, and in particular for treating exhaust gas emissions generated by power plants, gas turbines, lean burn internal combustion engines, and the like. Exhaust gas emissions are improved, at least in part, by reducing NO_x concentrations using catalysts that require infrequent regenerations.

Preferably, the catalyst composition includes a small pore molecular sieve having both nickel and at least one other metal, such as copper or iron, dispersed on and/or within the molecular sieve as extra-framework metal. Examples of suitable molecular sieves include aluminosilicates (zeolites), silicoaluminophosphates (SAPOs), aluminophosphates (AIPOs), and the like. Examples of preferred molecular sieves include zeolites and SAPOs having a small pore framework (i.e., having a maximum framework ring size of 8 tetrahedral units). Examples of small pore molecular sieves include those having a Framework Type Code selected from the group consisting of: ACO, AEI, AEN, AFN, AFT, AFX, ANA, APC, APD, ATT, CDO, CHA, DDR, DFT, EAB, EDI, EPI, ERI, GIS, GOO, IHW, ITE, ITW, LEV, KFI, MER, MON, NSI, OWE, PAU, PHI, RHO, RTH, SAT, SAV, SIV, THO, TSC, UEI, UFI, VNI, YUG and ZON. Particularly preferred frameworks include AEI, AFT, AFX, CHA, DDR, RHO, MER, LTA, UFI, RTH, SAV, PAU, LEV, ERI, and KFI, with SAV, CHA and AEI being particularly preferred. In a preferred embodiment, one or more of the small pore molecular sieves may comprise a CHA Framework Type Code selected from SAPO-34, AIPO-34, SAPO-47, ZYT-6, CAL-1, SAPO-40, SSZ-62 or SSZ-13, an SAV framework selected from SAPO-STA-7, and/or an AEI Framework Type Code of selected from AIPO-18, SAPO-18, SIZ-8, or SSZ-39. Useful mixed phase molecular sieves include AEI/CHA-mixed phase composition, such as a disordered AEI/CHA framework or an AEI/CHA intergrowth. The ratio of each framework type in the mixed phase molecular sieve is not particularly limited. For example, the ratio of AEI/CHA may range from about 5/95 to about 95/5, preferably about 60/40 to 40/60. In an exemplary embodiment, the ratio of AEI/CHA may range from about 5/95 to about 40/60. It will be appreciated that molecular sieves having a specific Framework Type Code include the all isotypic framework materials defined by that Framework Type Code.

As used herein the term "zeolite" means a synthetic aluminosilicate molecular sieve having a framework constructed of alumina and silica (i.e., repeating SiO_4 and AlO_4 tetrahedral units), and preferably having a molar silica-to-alumina ratio (SAR) of at least 10. Thus the term "zeolites" as used in the present invention do not include silica-aluminophosphates (SAPOs) and thus do not have an appreciable amount of phosphorous in their framework. That is, the zeolite frameworks do not have phosphorous as a regular repeating unit and/or do not have an amount of phosphorous that would affect the basic physical and/or chemical properties of the material, particularly with respect to the material's capacity to selectively reduce NO_x over a broad temperature range. In certain embodiments, the amount of framework phosphorous is less than 0.1 weight percent, preferably less than 0.01 or less than 0.001 weight percent, based on the total weight of the zeolite.

Zeolites, as used herein, are free or substantially free of framework metals, other than aluminum. Thus, a “zeolite” is distinct from a “metal-substituted zeolite” (also referred to as “isomorphous substituted zeolite”), wherein the latter comprises a framework that contains one or more non-aluminum metals substituted into the zeolite’s framework.

5 Preferred zeolites have a mole silica to alumina ratio (SAR) of less than about 50 and/or at least 10, more preferably about 10 to about 30, for example about 10 to about 25, from about 15 to about 20, from about 20 to about 30, or from about 5 to about 10. The silica-to-alumina ratio of zeolites may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid atomic framework of the zeolite crystal and to exclude silicon or aluminum in the binder or in
10 cationic or other form within the channels. Since it may be difficult to directly measure the silica to alumina ratio of zeolite after it has been combined with a binder material, particularly an alumina binder, these silica-to-alumina ratios are expressed in terms of the SAR of the zeolite per se, i.e., prior to the combination of the zeolite with the other catalyst components.

The bi-metal small pore molecular sieve catalysts of the present invention contain nickel and at
15 least one additional metal, wherein both the nickel and at least one additional metal (e.g., Cu or Fe) are present as extra-framework metals. As used herein, an “extra-framework metal” is one that resides within the molecular sieve and/or on at least a portion of the molecular sieve surface (preferably at an acid site on the molecular sieve), does not include aluminum, and does not include atoms constituting the framework of the molecular sieve. The nickel and at least one additional metal simultaneous and
20 synergistically resists deactivation by sulfur and also facilitates the treatment of exhaust gases, such as exhaust gas from a diesel engine, including processes such as NO_x reduction, NH₃ oxidation, and NO_x storage.

Preferred metals to be paired with nickel include transition metals such as copper, iron, zinc, tungsten, molybdenum, cobalt, titanium, zirconium, manganese, chromium, vanadium, niobium, as well
25 as tin, bismuth, and antimony. Other metals that may be used in combination with nickel include platinum group metals, such as ruthenium, rhodium, palladium, indium, platinum; precious metals such as gold and silver; and/or lanthanide metals such as cerium. Preferred transition metals are base metals, and preferred base metals include those selected from the group consisting of copper and iron. Preferred metals for storing NO_x and selective reduction of NO_x in exhaust gas include Cu and Fe.
30 Particularly useful metals for oxidizing CO, hydrocarbons, and/or ammonia are Pt and Pd. Particularly preferred combinations include nickel and copper or nickel and iron. Combinations of nickel and copper

or nickel and iron are particularly suited as extra-framework metals on molecular sieves, including those having a CHA or AEI framework.

In certain embodiments, the catalyst composition further comprises at least one alkali or alkaline earth metal, wherein the alkali or alkaline earth metal(s) are disposed on or within the molecular sieve material. The alkali or alkaline earth metal can be selected from sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, or some combination thereof. As used here, the phrase "alkali or alkaline earth metal" does not mean the alkali metals and alkaline earth metals are used in the alternative, but instead that one or more alkali metals can be used alone or in combination with one or more alkaline earth metals and that one or more alkaline earth metals can be used alone or in combination with one or more alkali metals. In certain embodiments, alkali metals are preferred. In certain embodiments, alkaline earth metals are preferred. Preferred alkali or alkaline earth metals include calcium, potassium, and combinations thereof. In certain embodiments, the catalyst composition is essentially free of magnesium and/or barium. In certain embodiments, the catalyst is essentially free of any alkali or alkaline earth metal except calcium and potassium. In certain embodiments, the catalyst is essentially free of any alkali or alkaline earth metal except calcium. As used herein, the term "essentially free" with respect to metal means that the material does not have an appreciable amount of the particular metal. That is, the particular metal is not present in amount that would affect the basic physical and/or chemical properties of the material, particularly with respect to the material's capacity to selectively reduce or store NO_x.

For some applications, the catalyst composition is free or essentially free of platinum group metals and precious metals. For some applications, the catalyst composition is free or essentially free of alkali metals. For some applications, the catalyst composition is free or essentially free of alkaline earth metals. For some applications, the catalyst composition is free or essentially free of transition metals except aluminum, nickel, copper, and iron. For some applications, the catalyst composition is free or essentially free of platinum group metals, precious metals, alkali and alkaline earth metals, lanthanum group metals, and transition metals except aluminum, nickel, and copper.

In certain embodiments, the total amount of non-aluminum transition metal present as extra-framework in the bi-metal molecular sieve ranges from about 0.1 to about 15 weight percent (wt%) based on the total weight of the molecular sieve, for example from about 2 wt% to about 10 wt%, about 4 to about 8 wt%, about 1 to about 5 wt%, or about 5 wt% to about 7 wt%. For embodiments which utilize copper, iron, or the combination thereof, the concentration of these transition metals in the

molecular sieve material is preferably about 1 to about 5 weight percent, more preferably about 2.5 to about 3.5 weight percent.

In certain embodiments, the total extra-framework transition metals (T_M) (i.e., including nickel) are present in an amount relative to the amount of aluminum in the molecular sieve (such as a zeolite), namely the framework aluminum. As used herein, the transition metal:aluminum (T_M :Al) ratio is based on the relative molar amount of promoter metal to molar framework Al in the corresponding zeolite. In certain embodiments, the catalyst material has a T_M :Al ratio of about 0.1 to about 1.0, preferably about 0.2 to about 0.5. A T_M :Al ratio of about 0.2 to about 0.5 is particularly useful where T_M is copper or iron, and more particularly where T_M is copper or iron and the SAR of the zeolite is about 15 - 30.

For certain applications, sulfur tolerance is dramatically improved by maintaining the ratio of Ni to the one or more other transition metal (T_M) in a range of about 10:1 to about 1:2. In certain embodiments, the ratio of Ni to the one or more other transition metal (T_M) is at least one. In certain other embodiments, the ratio of Ni to the one or more other transition metal (T_M) is about 2:1 to about 1:2, about 1.5:1 to about 1:1.5, about 1.2:1 to about 1:1.2, or about 1.1:1 to about 1:1.1.

Preferably, incorporation of at least a majority of the Ni and other metals such as Cu or Fe into the molecular sieve occurs during synthesis of the molecular sieve. The non-framework transition metal incorporated into the channels and/or cavities of a molecular sieve during its crystallization is referred to herein as *in-situ* metal. In general, the metal containing molecular sieves of the present invention are prepared from a one-pot synthesis admixture. This admixture contains a source of nickel, a source of additional transition metal, in addition to other components such as a source of silica, a source of alumina, a structure directing agent, and the like.

Polyamines, including comprising diethylenetriamine (DETA), N-(2-hydroxyethyl)ethylenediamine (HEEDA), triethylenetetramine (TETA), N,N'-bis(2-aminoethyl)-1,3-propanediamine (232), 1,2-bis(3-aminopropylamino)ethane (323), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), and Tetraamine are useful as chelating agents with Cu^{2+} and Ni^{2+} for the synthesis of SAPO-34 and SAPO-18. Other metallo-organic complexes useful for incorporating an extra-framework metal into the molecular sieve include metal-bipyridines, such as Cu bipyridine and Ni bipyridine.

In addition, metal salts can be used as a non-aluminum transition metal source. Examples of useful metal salts including nickel sulfate, copper sulfate, nickel acetate, and copper acetate. When metal salts are used in the reaction admixture, the salts preferably have similar cations, for example, nickel acetate and copper acetate or nickel sulfate and copper sulfate.

Suitable silica sources include, without limitation, fumed silica, silicates, precipitated silica, colloidal silica, silica gels, dealuminated zeolites such as dealuminated zeolite Y, and silicon hydroxides and alkoxides. Silica sources resulting in a high relative yield are preferred.

5 Typical alumina sources also are generally known and include aluminates, alumina, other zeolites, aluminum colloids, boehmites, pseudo-boehmites, aluminum hydroxides, aluminum salts such as aluminum sulfate and alumina chloride, aluminum hydroxides and alkoxides, alumina gels.

Suitable structure directing agents (SDAs) for directing the synthesis of a CHA framework-type material include adamantammonium compounds, such as N,N,N-trimethyl-1-adamantammonium compounds, N,N,N-trimethyl-2-adamantammonium compounds, and N,N,N-
10 trimethylcyclohexylammonium compounds, N,N-dimethyl-3,3-dimethylpiperidinium compounds, N,N-methylethyl-3,3-dimethylpiperidinium compounds, N,N-dimethyl-2-methylpiperidinium compounds, 1,3,3,6,6-pentamethyl-6-azonio-bicyclo(3.2.1)octane compounds, N,N-dimethylcyclohexylamine. Other SDAs include N,N,N-dimethylethylcyclohexylammonium (DMECHA), N,N,N-
15 methyl-diethylcyclohexylammonium (MDECHA), N,N,N-triethylcyclohexylammonium (TECHA), 2,7-dimethyl-1-azonium[5,4]decane (DM27AD), N-alkyl-3-quinuclidinol cations such as N-methyl-3-quinuclidinol, and N,N,N-trialkyl-exoaminonorborene cations. Representative anions include halogen, e.g., fluoride, chloride, bromide and iodide, hydroxide, acetate, sulfate, tetrafluoroborate, carboxylate, and the like. Hydroxide is the most preferred anion.

Examples of suitable templating agents for AEI include N,N-Diethyl-2,6-dimethylpiperidinium
20 cation; N,N-Dimethyl-9-azoniabicyclo 3.3.1nonane; N,N-Dimethyl-2,6-dimethylpiperidinium cation; N-Ethyl-N-methyl-2,6-dimethylpiperidinium cation; N,N-Diethyl-2-ethylpiperidinium cation; N,N-Dimethyl-2-(2-hydroxyethyl)piperidinium cation; N,N-Dimethyl-2-ethylpiperidinium cation; N,N-Dimethyl-3,5-dimethylpiperidinium cation; N-Ethyl-N-methyl-2-ethylpiperidinium cation; 2,6-Dimethyl-1-Azonium 5.4
25 decane cation; N-Ethyl-N-propyl-2,6-dimethylpiperidinium cation; 2,2,4,6,6-Pentamethyl-2-azoniabicyclo 3.2.1 octane cation; and N,N-Diethyl-2,5-dimethyl-2,5-dihydropyrrolium cation, with N,N-Dimethyl-3,5-dimethylpiperidinium or 1,1-Diethyl-2,6-dimethylpiperidinium being particularly preferred. The anion associated with the cation may be any anion which is not detrimental to the formation of the molecular sieve. Representative anions include halogen, e.g., fluoride, chloride, bromide and iodide, hydroxide, acetate, sulfate, tetrafluoroborate, carboxylate, and the like. Hydroxide is the most preferred anion. In
30 certain embodiments, the reaction mixture and subsequent molecular sieve is free or essentially free of fluorine.

One-pot synthesis is conducted by combining predetermined relative amounts of the admixture components under various mixing and heating regimens as will be readily apparent to those skilled in the art. Reaction temperatures, mixing times and speeds, and other process parameters that are suitable for conventional molecular sieve synthesis techniques are also generally suitable for the present invention. Hydrothermal crystallization is usually conducted under autogenous pressure, at a temperature of about 100 to 200 °C for a duration of several days, such about 1 – 20 days, a preferably about 1 – 3 days.

At the conclusion the crystallization period, the resulting solids are separated from the remaining reaction liquid by standard mechanical separation techniques, such as vacuum filtration. The recovered solids are then rinsed with deionized water, and dried at an elevated temperature (e.g., 75 – 150 °C) for several hours (e.g., about 4 to 24 hours). The drying step can be performed under vacuum or at atmospheric pressure.

The dried molecular sieve crystals are preferably calcined, but can also be used without calcination.

It will be appreciated that the foregoing sequence of steps, as well as each of the above-mentioned periods of time and temperature values are merely exemplary and may be varied.

The foregoing one-pot synthesis procedure permits adjusting the transition metal content of the crystals based on the composition of the starting synthesis mixture. For example, a desired Cu or Ni content can be directed by providing a predetermined relative amount of Cu or Ni source in the synthesis mixture, without requiring post synthesis impregnation or exchange to increase or decrease the metal loading on the material. In certain embodiments, the molecular sieve is free of post-synthesis exchanged metal, including copper, iron, and nickel.

The extra-frame transition metals, such as Cu and Ni, are catalytically active and uniformly dispersed within the molecular sieve framework. In certain embodiments, the extra-framework metals are uniformly dispersed if there is little to no bulk accumulation of the metals and/or there is little to no accumulation of the metals on the surface of the molecular sieve crystals. Accordingly, in one aspect of the invention, provided is a bi-metal molecular sieve having two or more extra-framework metals, wherein the weight percentage of extra-framework metal in the molecular sieve as measured by (X-ray photoelectron spectroscopy (XPS) is within 15%, more preferably 10%, of the weight percentage of the extra-framework metal in the molecular sieve as measured by either X-ray Fluorescence (XRF) or inductively coupled plasma (ICP) techniques.

In certain embodiments, a uniformly dispersed transition metal means that the molecular sieve contains not more than about 5 weight percent transition metal in the form of a transition metal oxide (e.g., CuO, FeO, Fe₂O₃, Fe₃O₄), also referred to herein as a free transition metal oxide, or a soluble transition metal oxide, relative to the total amount of that transition metal in the molecular sieve.

5 Preferably, the molecular sieve contains a majority of *in-situ* transition metal compared to free transition metal oxides. In certain embodiments, the molecular sieve contains a weight ratio of free transition metal oxides (e.g., CuO) to *in-situ* transition metal (e.g. ionic Cu) of less than about 1, less than about 0.5, less than about 0.1, or less than about 0.01, for example about 1 to about 0.001, about 0.5 to about 0.001, about 0.1 to about 0.001, or about 0.01 to about 0.001.

10 The molecular sieve catalyst can be used without a post-synthesis metal exchange. However, in certain embodiments, the molecular sieve undergoes a post-synthesis metal exchange. Thus, in certain embodiments, provided is a catalyst comprising a molecular sieve containing one or more catalytic metals exchanged into the channels and/or cavities of the molecular sieve post molecular sieve-
15 sieve synthesis in addition to *in-situ* nickel and copper or iron. Examples of metals that can be post-molecular sieve synthesis exchanged or impregnated include transition metals, including copper, nickel, zinc, iron, tungsten, molybdenum, cobalt, titanium, zirconium, manganese, chromium, vanadium, niobium, as well as tin, bismuth, and antimony; noble metals including platinum group metals (PGMs), such as ruthenium, rhodium, palladium, indium, platinum, and precious metals such as gold and silver; alkaline earth metals such as beryllium, magnesium, calcium, strontium, and barium; and rare earth metals such
20 as lanthanum, cerium, praseodymium, neodymium, europium, terbium, erbium, ytterbium, and yttrium. Preferred transition metals for post-synthesis exchange are base metals, and preferred base metals include those selected from the group consisting of manganese, iron, cobalt, nickel, and mixtures thereof. Metals incorporated post-synthesis can be added to the molecular sieve via any known technique such as ion exchange, impregnation, isomorphous substitution, etc. The amount of metal
25 post-synthesis exchanged can be from about 0.1 to about 3 weight percent, for example about 0.1 to about 1 weight percent, based on the total weight of the molecular sieve.

The foregoing one-pot synthesis procedure can result in molecular sieve crystals of uniform size and shape with relatively low amounts of agglomeration. In addition, the synthesis procedure can result in molecular sieve crystals having a mean crystalline size of about 0.1 to about 10 μm, for example about
30 0.5 to about 5 μm, about 0.1 to about 1 μm, about 1 to about 5 μm, about 3 to about 7 μm, and the like. In certain embodiments, large crystals are milled using a jet mill or other particle-on-particle milling

technique to an average size of about 1.0 to about 1.5 micron to facilitate washcoating a slurry containing the catalyst to a substrate, such as a flow-through monolith.

Crystal size is the length of one edge of a face of the crystal. Direct measurement of the crystal size can be performed using microscopy methods, such as SEM and TEM. Other techniques for determining mean particle size, such as laser diffraction and scattering can also be used. In addition to the mean crystal size, catalyst compositions preferably have a majority of the crystal sizes are greater than about 0.1 μm , preferably between about 0.5 and about 5 μm , such as about 0.5 to about 5 μm , about 0.7 to about 5 μm , about 1 to about 5 μm , about 1.5 to about 5.0 μm , about 1.5 to about 4.0 μm , about 2 to about 5 μm , or about 1 μm to about 10 μm .

Catalysts of the present invention are particularly applicable for heterogeneous catalytic reaction systems (i.e., solid catalyst in contact with a gas reactant). To improve contact surface area, mechanical stability, and/or fluid flow characteristics, the catalysts can be disposed on and/or within a substrate, preferably a porous substrate. In certain embodiments, a washcoat containing the catalyst is applied to an inert substrate, such as corrugated metal plate or a honeycomb cordierite brick.

Alternatively, the catalyst is kneaded along with other components such as fillers, binders, and reinforcing agents, into an extrudable paste which is then extruded through a die to form a honeycomb brick. Accordingly, in certain embodiments provided is a catalyst article comprising a bimetal molecular sieve catalyst described herein coated on and/or incorporated into a substrate.

Certain aspects of the invention provide a catalytic washcoat. The washcoat comprising the bimetal molecular sieve catalyst described herein is preferably a solution, suspension, or slurry. Suitable coatings include surface coatings, coatings that penetrate a portion of the substrate, coatings that permeate the substrate, or some combination thereof.

A washcoat can also include non-catalytic components, such as fillers, binders, stabilizers, rheology modifiers, and other additives, including one or more of alumina, silica, non-zeolite silica alumina, titania, zirconia, ceria. In certain embodiments, the catalyst composition may comprise pore-forming agents such as graphite, cellulose, starch, polyacrylate, and polyethylene, and the like. These additional components do not necessarily catalyze the desired reaction, but instead improve the catalytic material's effectiveness, for example, by increasing its operating temperature range, increasing contact surface area of the catalyst, increasing adherence of the catalyst to a substrate, etc. In preferred embodiments, the washcoat loading is $>0.3 \text{ g/in}^3$, such as $>1.2 \text{ g/in}^3$, $>1.5 \text{ g/in}^3$, $>1.7 \text{ g/in}^3$ or $>2.00 \text{ g/in}^3$, and preferably $< 3.5 \text{ g/in}^3$, such as $< 2.5 \text{ g/in}^3$. In certain embodiments, the washcoat is applied to a substrate in a loading of about 0.8 to 1.0 g/in^3 , 1.0 to 1.5 g/in^3 , or 1.5 to 2.5 g/in^3 .

Two of the most common substrate designs are plate and honeycomb. Preferred substrates, particularly for mobile applications, include flow-through monoliths having a so-called honeycomb geometry that comprise multiple adjacent, parallel channels that are open on both ends and generally extend from the inlet face to the outlet face of the substrate and result in a high-surface area-to-volume ratio. For certain applications, the honeycomb flow-through monolith preferably has a high cell density, for example about 600 to 800 cells per square inch, and/or an average internal wall thickness of about 0.18 – 0.35 mm, preferably about 0.20 – 0.25 mm. For certain other applications, the honeycomb flow-through monolith preferably has a low cell density of about 150 – 600 cells per square inch, more preferably about 200 – 400 cells per square inch. Preferably, the honeycomb monoliths are porous. In addition to cordierite, silicon carbide, silicon nitride, ceramic, and metal, other materials that can be used for the substrate include aluminum nitride, silicon nitride, aluminum titanate, α -alumina, mullite, e.g., acicular mullite, pollucite, a thermet such as Al_2OsZFe , $\text{Al}_2\text{O}_3/\text{Ni}$ or B_4CZFe , or composites comprising segments of any two or more thereof. Preferred materials include cordierite, silicon carbide, and alumina titanate.

Plate-type catalysts have lower pressure drops and are less susceptible to plugging and fouling than the honeycomb types, which is advantageous in high efficiency stationary applications, but plate configurations can be much larger and more expensive. A Honeycomb configuration is typically smaller than a plate type, which is an advantage in mobile applications, but has higher pressure drops and plug more easily. In certain embodiments the plate substrate is constructed of metal, preferably corrugated metal.

In certain embodiments, the invention is a catalyst article made by a process described herein. In a particular embodiment, the catalyst article is produced by a process that includes the steps of applying a bi-metal molecular sieve catalyst composition, preferably as a washcoat, to a substrate as a layer either before or after at least one additional layer of another composition for treating exhaust gas has been applied to the substrate. The one or more catalyst layers on the substrate, including the bi-metal molecular sieve catalyst layer, are arranged in consecutive layers. As used herein, the term “consecutive” with respect to catalyst layers on a substrate means that each layer is contact with its adjacent layer(s) and that the catalyst layers as a whole are arranged one on top of another on the substrate.

In certain embodiments, the bi-metal molecular sieve catalyst is disposed on the substrate as a first layer and another composition, such as an oxidation catalyst, reduction catalyst, scavenging component, or NO_x storage component, is disposed on the substrate as a second layer. In other

embodiments, the bi-metal molecular sieve catalyst is disposed on the substrate as a second layer and another composition, such as such as an oxidation catalyst, reduction catalyst, scavenging component, or NO_x storage component, is disposed on the substrate as a first layer. As used herein the terms “first layer” and “second layer” are used to describe the relative positions of catalyst layers in the catalyst article with respect to the normal direction of exhaust gas flow-through, past, and/or over the catalyst article. Under normal exhaust gas flow conditions, exhaust gas contacts the first layer prior to contacting the second layer. In certain embodiments, the second layer is applied to an inert substrate as a bottom layer and the first layer is top layer that is applied over the second layer as a consecutive series of sub-layers. In such embodiments, the exhaust gas penetrates (and hence contacts) the first layer, before contacting the second layer, and subsequently returns through the first layer to exit the catalyst component. In other embodiments, the first layer is a first zone disposed on an upstream portion of the substrate and the second layer is disposed on the substrate as a second zone, wherein the second zone is downstream of the first.

In another embodiment, the catalyst article is produced by a process that includes the steps of applying a bi-metal molecular sieve catalyst composition, preferably as a washcoat, to a substrate as a first zone, and subsequently applying at least one additional composition for treating an exhaust gas to the substrate as a second zone, wherein at least a portion of the first zone is downstream of the second zone. Alternatively, the bi-metal molecular sieve catalyst composition can be applied to the substrate in a second zone that is downstream of a first zone containing the additional composition. Examples of additional compositions include oxidation catalysts, reduction catalysts, scavenging components (e.g., for sulfur, water, etc.), or NO_x storage components.

To reduce the amount of space required for an exhaust system, individual exhaust components in certain embodiments are designed to perform more than one function. For example, applying an SCR catalyst to a wall-flow filter substrate instead of a flow-through substrate serves to reduce the overall size of an exhaust treatment system by allowing one substrate to serve two functions, namely catalytically reducing NO_x concentration in the exhaust gas and mechanically removing soot from the exhaust gas. Accordingly, in certain embodiments, the substrate is a honeycomb wall-flow filter or partial filter. Wall-flow filters are similar to flow-through honeycomb substrates in that they contain a plurality of adjacent, parallel channels. However, the channels of flow-through honeycomb substrates are open at both ends, whereas the channels of wall-flow substrates have one end capped, wherein the capping occurs on opposite ends of adjacent channels in an alternating pattern. Capping alternating ends of channels prevents the gas entering the inlet face of the substrate from flowing straight through

the channel and existing. Instead, the exhaust gas enters the front of the substrate and travels into about half of the channels where it is forced through the channel walls prior to entering the second half of the channels and exiting the back face of the substrate.

5 The substrate wall has a porosity and pore size that is gas permeable, but traps a major portion of the particulate matter, such as soot, from the gas as the gas passes through the wall. Preferred wall-flow substrates are high efficiency filters. Wall flow filters for use with the present invention preferably have an efficiency of least 70%, at least about 75%, at least about 80%, or at least about 90%. In certain
10 embodiments, the efficiency will be from about 75 to about 99%, about 75 to about 90%, about 80 to about 90%, or about 85 to about 95%. Here, efficiency is relative to soot and other similarly sized particles and to particulate concentrations typically found in conventional diesel exhaust gas. For example, particulates in diesel exhaust can range in size from 0.05 microns to 2.5 microns. Thus, the efficiency can be based on this range or a sub-range, such as 0.1 to 0.25 microns, 0.25 to 1.25 microns, or 1.25 to 2.5 microns.

15 Porosity is a measure of the percentage of void space in a porous substrate and is related to backpressure in an exhaust system: generally, the lower the porosity, the higher the backpressure. Preferably, the porous substrate has a porosity of about 30 to about 80%, for example about 40 to about 75%, about 40 to about 65%, or from about 50 to about 60%.

20 The pore interconnectivity, measured as a percentage of the substrate's total void volume, is the degree to which pores, void, and/or channels, are joined to form continuous paths through a porous substrate, i.e., from the inlet face to the outlet face. In contrast to pore interconnectivity is the sum of closed pore volume and the volume of pores that have a conduit to only one of the surfaces of the substrate. Preferably, the porous substrate has a pore interconnectivity volume of at least about 30%, more preferably at least about 40%.

25 The mean pore size of the porous substrate is also important for filtration. Mean pore size can be determined by any acceptable means, including by mercury porosimetry. The mean pore size of the porous substrate should be of a high enough value to promote low backpressure, while providing an adequate efficiency by either the substrate per se, by promotion of a soot cake layer on the surface of the substrate, or combination of both. Preferred porous substrates have a mean pore size of about 10 to about 40 μm , for example about 20 to about 30 μm , about 10 to about 25 μm , about 10 to about
30 20 μm , about 20 to about 25 μm , about 10 to about 15 μm , and about 15 to about 20 μm .

In general, the production of an extruded solid body containing the bi-metal molecular sieve catalyst involves blending the bi-metal molecular sieve catalyst, a binder, an optional organic viscosity-

enhancing compound into an homogeneous paste which is then added to a binder/matrix component or a precursor thereof and optionally one or more of stabilized ceria, and inorganic fibers. The blend is compacted in a mixing or kneading apparatus or an extruder. The mixtures have organic additives such as binders, pore formers, plasticizers, surfactants, lubricants, dispersants as processing aids to enhance wetting and therefore produce a uniform batch. The resulting plastic material is then molded, in particular using an extrusion press or an extruder including an extrusion die, and the resulting moldings are dried and calcined. The organic additives are "burnt out" during calcinations of the extruded solid body. A bi-metal molecular sieve catalyst may also be washcoated or otherwise applied to the extruded solid body as one or more sub-layers that reside on the surface or penetrate wholly or partly into the extruded solid body.

Extruded solid bodies containing bi-metal molecular sieve catalysts according to the present invention generally comprise a unitary structure in the form of a honeycomb having uniform-sized and parallel channels extending from a first end to a second end thereof. Channel walls defining the channels are porous. Typically, an external "skin" surrounds a plurality of the channels of the extruded solid body. The extruded solid body can be formed from any desired cross section, such as circular, square or oval. Individual channels in the plurality of channels can be square, triangular, hexagonal, circular etc. Channels at a first, upstream end can be blocked, e.g. with a suitable ceramic cement, and channels not blocked at the first, upstream end can also be blocked at a second, downstream end to form a wall-flow filter. Typically, the arrangement of the blocked channels at the first, upstream end resembles a checker-board with a similar arrangement of blocked and open downstream channel ends.

The binder/matrix component is preferably selected from the group consisting of cordierite, nitrides, carbides, borides, intermetallics, lithium aluminosilicate, a spinel, an optionally doped alumina, a silica source, titania, zirconia, titania-zirconia, zircon and mixtures of any two or more thereof. The paste can optionally contain reinforcing inorganic fibers selected from the group consisting of carbon fibers, glass fibers, metal fibers, boron fibers, alumina fibers, silica fibers, silica-alumina fibers, silicon carbide fibers, potassium titanate fibers, aluminum borate fibers and ceramic fibers.

The alumina binder/matrix component is preferably gamma alumina, but can be any other transition alumina, i.e., alpha alumina, beta alumina, chi alumina, eta alumina, rho alumina, kappa alumina, theta alumina, delta alumina, lanthanum beta alumina and mixtures of any two or more such transition aluminas. It is preferred that the alumina is doped with at least one non-aluminum element to increase the thermal stability of the alumina. Suitable alumina dopants include silicon, zirconium,

barium, lanthanides and mixtures of any two or more thereof. Suitable lanthanide dopants include La, Ce, Nd, Pr, Gd and mixtures of any two or more thereof.

Sources of silica can include a silica sol, quartz, fused or amorphous silica, sodium silicate, an amorphous aluminosilicate, an alkoxysilane, a silicone resin binder such as methylphenyl silicone resin, a clay, talc or a mixture of any two or more thereof. Of this list, the silica can be SiO₂ as such, feldspar, mullite, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, ternary silica-alumina-zirconia, ternary silica-alumina-magnesia, ternary-silica-magnesia-zirconia, ternary silica-alumina-thoria and mixtures of any two or more thereof.

Preferably, the bi-metal molecular sieve catalyst is dispersed throughout, and preferably evenly throughout, the entire extruded catalyst body.

Where any of the above extruded solid bodies are made into a wall-flow filter, the porosity of the wall-flow filter can be from 30-80%, such as from 40-70%. Porosity and pore volume and pore radius can be measured e.g. using mercury intrusion porosimetry.

The bi-metal molecular sieve catalyst described herein can promote the reaction of a reductant, preferably ammonia, with nitrogen oxides to selectively form elemental nitrogen (N₂) and water (H₂O). Thus, in one embodiment, the catalyst can be formulated to favor the reduction of nitrogen oxides with a reductant (i.e., an SCR catalyst). Examples of such reductants include hydrocarbons (e.g., C₃ – C₆ hydrocarbons) and nitrogenous reductants such as ammonia and ammonia hydrazine or any suitable ammonia precursor, such as urea ((NH₂)₂CO), ammonium carbonate, ammonium carbamate, ammonium hydrogen carbonate or ammonium formate.

The bi-metal molecular sieve catalyst described herein can also promote the oxidation of ammonia. Thus, in another embodiment, the catalyst can be formulated to favor the oxidation of ammonia with oxygen, particularly a concentrations of ammonia typically encountered downstream of an SCR catalyst (e.g., ammonia oxidation (AMOX) catalyst, such as an ammonia slip catalyst (ASC)). In certain embodiments, the bi-metal molecular sieve catalyst is disposed as a top layer over an oxidative under-layer, wherein the under-layer comprises a platinum group metal (PGM) catalyst or a non-PGM catalyst. Preferably, the catalyst component in the underlayer is disposed on a high surface area support, including but not limited to alumina.

In yet another embodiment, an SCR and AMOX operations are performed in series, wherein both processes utilize a catalyst comprising the bi-metal molecular sieve catalyst described herein, and wherein the SCR process occurs upstream of the AMOX process. For example, an SCR formulation of the

catalyst can be disposed on the inlet side of a filter and an AMOX formulation of the catalyst can be disposed on the outlet side of the filter.

Accordingly, provided is a method for the reduction of NO_x compounds or oxidation of NH_3 in a gas, which comprises contacting the gas with a catalyst composition described herein for the catalytic reduction of NO_x compounds for a time sufficient to reduce the level of NO_x compounds and/or NH_3 in the gas. In certain embodiments, provided is a catalyst article having an ammonia slip catalyst disposed downstream of a selective catalytic reduction (SCR) catalyst. In such embodiments, the ammonia slip catalyst oxidizes at least a portion of any nitrogenous reductant that is not consumed by the selective catalytic reduction process. For example, in certain embodiments, the ammonia slip catalyst is disposed on the outlet side of a wall flow filter and an SCR catalyst is disposed on the upstream side of a filter. In certain other embodiments, the ammonia slip catalyst is disposed on the downstream end of a flow-through substrate and an SCR catalyst is disposed on the upstream end of the flow-through substrate. In other embodiments, the ammonia slip catalyst and SCR catalyst are disposed on separate bricks within the exhaust system. These separate bricks can be adjacent to, and in contact with, each other or separated by a specific distance, provided that they are in fluid communication with each other and provided that the SCR catalyst brick is disposed upstream of the ammonia slip catalyst brick.

In certain embodiments, the SCR and/or AMOX process is performed at a temperature of at least 100°C . In another embodiment, the process(es) occur at a temperature from about 150°C to about 750°C . In a particular embodiment, the temperature range is from about 175 to about 550°C . In another embodiment, the temperature range is from 175 to 400°C . In yet another embodiment, the temperature range is 450 to 900°C , preferably 500 to 750°C , 500 to 650°C , 450 to 550°C , or 650 to 850°C . Embodiments utilizing temperatures greater than 450°C are particularly useful for treating exhaust gases from a heavy and light duty diesel engine that is equipped with an exhaust system comprising (optionally catalyzed) diesel particulate filters which are regenerated actively, e.g. by injecting hydrocarbon into the exhaust system upstream of the filter, wherein the molecular sieve catalyst for use in the present invention is located downstream of the filter.

According to another aspect of the invention, provided is a method for the reduction of NO_x compounds and/or oxidation of NH_3 in a gas, which comprises contacting the gas with a catalyst described herein for a time sufficient to reduce the level of NO_x compounds in the gas. Methods of the present invention may comprise one or more of the following steps: (a) accumulating and/or combusting soot that is in contact with the inlet of a catalytic filter; (b) introducing a nitrogenous reducing agent into the exhaust gas stream prior to contacting the catalytic filter, preferably with no

intervening catalytic steps involving the treatment of NO_x and the reductant; (c) generating NH₃ over a NO_x adsorber catalyst or lean NO_x trap, and preferably using such NH₃ as a reductant in a downstream SCR reaction; (d) contacting the exhaust gas stream with a DOC to oxidize hydrocarbon based soluble organic fraction (SOF) and/or carbon monoxide into CO₂, and/or oxidize NO into NO₂, which in turn, may
5 be used to oxidize particulate matter in particulate filter; and/or reduce the particulate matter (PM) in the exhaust gas; (e) contacting the exhaust gas with one or more flow-through SCR catalyst device(s) in the presence of a reducing agent to reduce the NO_x concentration in the exhaust gas; and (f) contacting the exhaust gas with an ammonia slip catalyst, preferably downstream of the SCR catalyst to oxidize most, if not all, of the ammonia prior to emitting the exhaust gas into the atmosphere or passing the
10 exhaust gas through a recirculation loop prior to exhaust gas entering/re-entering the engine.

In another embodiment, all or at least a portion of the nitrogen-based reductant, particularly NH₃, for consumption in the SCR process can be supplied by a NO_x adsorber catalyst (NAC), a lean NO_x trap (LNT), or a NO_x storage/reduction catalyst (NSRC), disposed upstream of the SCR catalyst, e.g., a SCR catalyst of the present invention disposed on a wall-flow filter. NAC components useful in the
15 present invention include a catalyst combination of a basic material (such as alkali metal, alkaline earth metal or a rare earth metal, including oxides of alkali metals, oxides of alkaline earth metals, and combinations thereof), and a precious metal (such as platinum), and optionally a reduction catalyst component, such as rhodium. Specific types of basic material useful in the NAC include cesium oxide, potassium oxide, magnesium oxide, sodium oxide, calcium oxide, strontium oxide, barium oxide, and
20 combinations thereof. The precious metal is preferably present at about 10 to about 200 g/ft³, such as 20 to 60 g/ft³. Alternatively, the precious metal of the catalyst is characterized by the average concentration which may be from about 40 to about 100 grams/ft³.

Under certain conditions, during the periodically rich regeneration events, NH₃ may be generated over a NO_x adsorber catalyst. The SCR catalyst downstream of the NO_x adsorber catalyst may
25 improve the overall system NO_x reduction efficiency. In the combined system, the SCR catalyst is capable of storing the released NH₃ from the NAC catalyst during rich regeneration events and utilizes the stored NH₃ to selectively reduce some or all of the NO_x that slips through the NAC catalyst during the normal lean operation conditions.

The method for treating exhaust gas as described herein can be performed on an exhaust gas
30 derived from a combustion process, such as from an internal combustion engine (whether mobile or stationary), a gas turbine and coal or oil fired power plants. The method may also be used to treat gas from industrial processes such as refining, from refinery heaters and boilers, furnaces, the chemical

processing industry, coke ovens, municipal waste plants and incinerators, etc. In a particular embodiment, the method is used for treating exhaust gas from a vehicular lean burn internal combustion engine, such as a diesel engine, a lean-burn gasoline engine or an engine powered by liquid petroleum gas or natural gas.

5 In certain aspects, the invention is a system for treating exhaust gas generated by combustion process, such as from an internal combustion engine (whether mobile or stationary), a gas turbine, coal or oil fired power plants, and the like. Such systems include a catalytic article comprising the bi-metal molecular sieve catalyst described herein and at least one additional component for treating the exhaust gas, wherein the catalytic article and at least one additional component are designed to function as a
10 coherent unit.

 In certain embodiments, the system comprises a catalytic article comprising a bi-metal molecular sieve catalyst described herein, a conduit for directing a flowing exhaust gas, a source of nitrogenous reductant disposed upstream of the catalytic article. The system can include a controller for the metering the nitrogenous reductant into the flowing exhaust gas only when it is determined that
15 the molecular sieve catalyst is capable of catalyzing NO_x reduction at or above a desired efficiency, such as at above 100 °C, above 150 °C or above 175 °C. The metering of the nitrogenous reductant can be arranged such that 60% to 200% of theoretical ammonia is present in exhaust gas entering the SCR catalyst calculated at 1:1 NH₃/NO and 4:3 NH₃/NO₂.

 In another embodiment, the system comprises an oxidation catalyst (e.g., a diesel oxidation
20 catalyst (DOC)) for oxidizing nitrogen monoxide in the exhaust gas to nitrogen dioxide can be located upstream of a point of metering the nitrogenous reductant into the exhaust gas. In one embodiment, the oxidation catalyst is adapted to yield a gas stream entering the SCR molecular sieve catalyst having a ratio of NO to NO₂ of from about 4:1 to about 1:3 by volume, e.g. at an exhaust gas temperature at oxidation catalyst inlet of 250 °C to 450 °C. The oxidation catalyst can include at least one platinum
25 group metal (or some combination of these), such as platinum, palladium, or rhodium, coated on a flow-through monolith substrate. In one embodiment, the at least one platinum group metal is platinum, palladium or a combination of both platinum and palladium. The platinum group metal can be supported on a high surface area washcoat component such as alumina, a zeolite such as an aluminosilicate zeolite, silica, non-zeolite silica alumina, ceria, zirconia, titania or a mixed or composite
30 oxide containing both ceria and zirconia.

 In a further embodiment, a suitable filter substrate is located between the oxidation catalyst and the SCR catalyst. Filter substrates can be selected from any of those mentioned above, e.g. wall flow

filters. Where the filter is catalyzed, e.g. with an oxidation catalyst of the kind discussed above, preferably the point of metering nitrogenous reductant is located between the filter and the molecular sieve catalyst. Alternatively, if the filter is un-catalyzed, the means for metering nitrogenous reductant can be located between the oxidation catalyst and the filter.

5 The catalysts of the present invention are less susceptible to sulfur poisoning compared to conventional catalysts. The catalyst's ability to maintain good catalytic activity when exposed to high levels of sulfur allows the catalyst to undergo less frequent regenerations to remove sulfur contaminants. Less frequent catalyst regenerations allow for more stable catalyst functionality and improved fuel economy. Conventional zeolite-based catalyst, such as copper zeolites, typically require
10 regeneration, e.g., at elevated temperatures above 500 °C, before sulfur contaminants reach 0.5 g per liter of catalysts. The bi-metal catalysts of the present invention can forego regeneration until sulfur concentrations on the catalyst are greater than 0.5 g / L of catalyst. Accordingly, in one aspect, the invention pertains to a method for regenerating an exhaust gas treatment catalyst comprising
15 contacting the bi-metal catalyst with an exhaust gas stream containing sulfur, and regenerating the bi-metal catalyst when the sulfur concentration on the catalyst is > 0.5 g sulfur / L of catalyst, for example, > 0.75 g sulfur / L of catalyst, > 1.0 g sulfur / L of catalyst, or > 1.5 g sulfur / L of catalyst.

In addition, the bi-metal catalyst is ideally suited to treat exhaust gas generated by combusting high sulfur ("dirty") fuel. Clean fuels, such as methane, typically have a sulfur content less than 0.5 ppm. Low sulfur gasoline typically has a sulfur content of about 5 ppm. Higher sulfur fuels can have a sulfur
20 content of greater than 10 ppm sulfur, for example, 50 ppm or 100 ppm. Accordingly, in one aspect, the invention pertains to a method for treating exhaust gas comprising containing the bi-metal catalyst with an exhaust gas stream containing > 10 ppm sulfur, for example > 25 ppm sulfur, > 50 ppm sulfur, > 75 ppm sulfur, or > 100 ppm sulfur.

The invention can also be defined according to one or more of the following definitions:

- 25 (i) A catalyst composition comprising a small pore molecular sieve, about 0.5 - 5 weight percent of a transition metal (T_M) selected from copper and/or iron, based on the total weight of the molecular sieve, and about 0.5 - 5 weight percent nickel, based on the total weight of the molecular sieve, wherein the transition metal and nickel are present in a T_M :Ni ratio of about 10:1 to about 1:2.
- (ii) The catalyst composition of (i), wherein the transition metal and the nickel are incorporated into the
30 molecular sieve during synthesis.
- (iii) The catalyst composition of (i), wherein a majority of the transition metal and the nickel are present as extra-framework metals.

- (iv) The catalyst composition of (i), wherein the molecular sieve is composed of crystals, and the transition metal and the nickel are present in a weight percentage as measured by XPS that is within 10% of their weight percentage as measured by XRF
- (v) The catalyst composition of (i), wherein the molecular sieve has a CHA framework.
- 5 (vi) The catalyst composition of (i), wherein the molecular sieve has an AEI framework.
- (vii) The catalyst composition of (i), wherein the molecular sieve is a zeolite having a silica-to-alumina ratio of about 10 to about 50.
- (viii) The catalyst composition of (i), wherein the molecular sieve is essentially free of non-aluminum framework metals.
- 10 (ix) The catalyst composition of (i), wherein the molecular sieve has a mean crystal size of about 0.5 to 5 microns.
- (x) The catalyst composition of (i), wherein the molecular sieve is essentially free of any post-synthesis exchanged metal.
- (xi) A method for synthesizing a molecular sieve comprising:
- 15 heating an admixture comprising a source of silica, a source of alumina, optionally a source of phosphate, a source of copper and/or iron, a source of nickel, and at least one structure directing agent to form zeolite crystals containing nickel and at least one of copper and iron, and separating the molecular sieve crystals from the mother liquor.
- 20 (xii) The method of (xi), wherein the copper and/or iron and the nickel are separately in the form of a metal salt when added to the admixture.
- (xiii) The method of (xi), wherein the copper and/or iron and the nickel are separately in the form of a metallo-organic complex comprising at least one organic constituent selected from diethylenetriamine (DETA); N-(2-hydroxyethyl)ethylenediamine (HEEDA); triethylenetetramine (TETA); N,N'-bis(2-aminoethyl)-1,3-propanediamine (232); 1,2-bis(3-aminopropylamino)ethane (323);
- 25 tetraethylenepentamine (TEPA); pentaethylenehexamine (PEHA); Tetraamine; and bipyridine.
- (xiv) A catalyst article comprising a substrate coated with a catalyst composition according to (i).
- (xv) The catalyst article of (xiv), wherein the substrate is a metal flow-through substrate, a honeycomb flow-through substrate, a honeycomb wall-flow filter, or a honeycomb partial filter.
- 30 (xvi) The catalyst article of (xv), wherein the coating is at least partially a surface coating.
- (xvii) The catalyst article of (xv), wherein the coating at least partially permeates into the substrate.

- (xviii) The catalyst article of (xv), wherein the coating is disposed as one or more zones and/or layers on the substrate.
- (xix) The catalyst article of (xv), further comprising a second coating comprising an oxidation catalyst.
- (xx) A catalyst article comprises a substrate formed from an extrudable composition comprising a catalyst composition according to (i).
- 5 (xxi) The catalyst article of (xix), further comprising a catalyst coating.
- (xxii) An SCR catalyst comprising a small pore molecular sieve, about 0.5 - 5 weight percent of a transition metal (T_M) selected from copper and/or iron, based on the total weight of the zeolite, and about 0.5 - 5 weight percent nickel, based on the total weight of the zeolite, wherein the transition
- 10 metal and nickel are present in a T_M :Ni ratio of about 10:1 to about 1:2, and wherein the catalyst is effective for reducing NO_x to N₂ in the presence of a reductant.
- (xxiii) A method for treating an exhaust gas comprising contacting a gas comprising NO_x and a reductant with a catalyst according to (i) to catalytically reduce at least a portion of the NO_x to N₂.
- (xxiv) The method of (xxiii), wherein the exhaust gas further comprises a source of sulfur.
- 15 (xxv) The method of (xxiii), wherein the exhaust gas comprises at least 10 ppm sulfur.
- (xxvi) A system for treating an exhaust gas comprising a catalyst article according to (xiv) and a source of reductant.
- (xxvii) The system of (xxvi), wherein the source of reductant is an ammonia or ammonia precursor injector, a HC injector, or a NO_x absorber catalyst.
- 20 (xxviii) The system of (xxvi), further comprising an oxidation catalyst upstream of the catalyst article.
- (xxix) The system of (xxvi), further comprising an engine manifold and a second SCR catalyst disposed downstream of the catalyst article, provided that there are no SCR catalysts disposed between the engine manifold and the catalyst article.
- (xxx) The system of (xxvi), further comprising a particulate filter.
- 25 (xxxi) The system of (xxvi), further comprising an ammonia slip catalyst.
- (xxxii) The system of (xxvi), further comprising a NO_x absorber catalyst.
- (xxxiii) The system of (xxvi), wherein the SCR catalyst is close coupled to an engine manifold and there are no catalysts for treating exhaust gas positioned between the manifold and the catalyst article.
- (xxiv) A method for regenerating a catalyst comprising:
- 30 contacting a catalyst composition according to (i) with an exhaust gas stream containing sulfur; and

regenerating the catalyst composition after the sulfur concentration on the catalyst is > 0.5 grams sulfur / liter of catalyst.

EXAMPLES

5 Prophetic Examples 1 – 8:

A series of polyamines comprising diethylenetriamine (DETA), N-(2-hydroxyethyl)ethylenediamine (HEEDA), triethylenetetramine (TETA), N,N'-bis(2-aminoethyl)-1,3-propanediamine (232), 1,2-bis(3-aminopropylamino)ethane (323), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), will be used as chelating agents with both Cu²⁺ and Ni²⁺ for the synthesis of SAPO-34 or SAPO-18. In a typical preparation, fumed silica will be added to an aluminophosphate gel prepared by mixing Al(OH)₃·H₂O (Aldrich, technical grade) with H₃PO₄ (BDH, 85%) in water, followed by addition of the copper or nickel complex, pre-prepared by adding copper acetate or nickel acetate to an aqueous solution of the polyamine. A portion of the total water content will be set aside for this purpose. Finally an excess of the same polyamine (so that the polyamine / M²⁺ ratio was 4 / 1) will be added dropwise to adjust the gel pH to 7. Cu-SAPO-18 will be prepared adopting specific conditions. Cu²⁺-N,N'-bis(2-aminoethyl)-1,3-propanediamine (232) will be used as the SDA while tetraethylammonium hydroxide (TEAOH), will be added dropwise to adjust the gel pH to 7. The overall gel composition is Al(OH)₃ : 0.61 H₃PO₄ : 0.2 SiO₂ : 40 H₂O : 0.05 Cu-232 : 0.27 TEOH. Seeds of STA-7, 1% weight in respect to the SiO₂ content, will be added to promote the nucleation of pure SAPO-18, because the two structures have a crystal plane in common. Details are given in Table 1

The final gels will be stirred continuously at room temperature until homogeneous, prior to being transferred to a Teflon-lined stainless steel autoclave and heated at 190 °C for 6 days. The resultant products will be suspended in water and sonicated to force separation of crystalline from fine grained amorphous solid, which was removed by decanting. Then, the crystalline materials will be collected by filtration, washed with deionized H₂O, and dried in air at 80 °C for 12 hours.

TABLE 1

Example No.	Polyamine	Metal	Co-base	Product (by XRD)
1	DETA	Cu ²⁺ / Ni ²⁺	DETA	SAPO-34
2	HEEDA	Cu ²⁺ / Ni ²⁺	HEEDA	SAPO-34
3	TETA	Cu ²⁺ / Ni ²⁺	TETA	SAPO-34/SAPO-18

Example No.	Polyamine	Metal	Co-base	Product (by XRD)
4	232	Cu ²⁺ / Ni ²⁺	232	SAPO-18
5	232	Cu ²⁺ / Ni ²⁺	TEAOH	AEI/CHA intergrowth
6	323	Cu ²⁺ / Ni ²⁺	323	SAPO-34
7	TEPA	Cu ²⁺ / Ni ²⁺	TEPA	AEI/CHA intergrowth
8	PEHA	Cu ²⁺ / Ni ²⁺	PEHA	AEI/CHA intergrowth

Example 9:

Powder samples of Cu-CHA (4.5 wt%Cu) and Cu,Ni-CHA (3.6 wt%Cu, 3.31wt%Ni) were prepared both with metal present during the synthesis process. Samples were evaluated for NO_x conversion at a space velocity of 30,000 h⁻¹, an ammonia to NO_x ratio of 1, and in NO only conditions before sulfation and twice after sulfation. The Cu-CHA sample (Figure 1, solid bars) shows the highest initial NO_x conversion, but drops 13% at 200 °C after exposure to 20 ppm of SO₂ for 35 min at 250 °C. The Cu,Ni (Figure 1, cross hatched bars) shows less than a 1% change over the sulfation and desulfation process. This stability should enable systems with less frequent regenerations.

10

CLAIMS:

1. A catalyst composition comprising a small pore molecular sieve, 0.5 - 5 weight percent of a transition metal (T_M) selected from copper and/or iron, based on the total weight of the molecular sieve, and 0.5 - 5 weight percent nickel, based on the total weight of the molecular sieve, wherein the transition metal and nickel are present in a T_M :Ni ratio of 10:1 to 1:2.
2. The catalyst composition according to claim 1, wherein the transition metal and the nickel are incorporated into the molecular sieve during synthesis.
3. The catalyst composition according to claim 1 or 2, wherein a majority of the transition metal and the nickel are present as extra-framework metals.
4. The catalyst composition according to claim 1, 2 or 3, wherein the molecular sieve is composed of crystals, and the transition metal and the nickel are present in a weight percentage as measured by XPS that is within 10% of their weight percentage as measured by XRF
5. The catalyst composition according to any preceding claim, wherein the molecular sieve has a CHA framework.
6. The catalyst composition according to any of claims 1 to 4, wherein the molecular sieve has an AEI framework.
7. The catalyst composition according to any preceding claim, wherein the molecular sieve is a zeolite having a silica-to-alumina ratio of 10 to 50.
8. The catalyst composition according to any preceding claim, wherein the molecular sieve is essentially free of non-aluminum framework metals.
9. The catalyst composition according to any preceding claim, wherein the molecular sieve is essentially free of any post-synthesis exchanged metal.
10. A method for synthesizing a molecular sieve comprising:
 - heating an admixture comprising a source of silica, a source of alumina, optionally a source of phosphate, a source of copper and/or iron, a source of nickel, and at least one structure directing agent to form zeolite crystals containing nickel and at least one of copper and iron, and
 - separating the molecular sieve crystals from the mother liquor.
11. A catalyst article comprising a substrate coated with a catalyst composition according to any of claims 1 to 9.
12. An SCR catalyst comprising a small pore molecular sieve, 0.5 - 5 weight percent of a transition metal (T_M) selected from copper and/or iron, based on the total weight of the zeolite, and 0.5 - 5 weight

percent nickel, based on the total weight of the zeolite, wherein the transition metal and nickel are present in a $T_M:Ni$ ratio of 10:1 to 1:2, and wherein the catalyst is effective for reducing NO_x to N_2 in the presence of a reductant.

13. A method for treating an exhaust gas comprising contacting a gas comprising NO_x and a reductant with a catalyst according to any of claims 1 to 9 to catalytically reduce at least a portion of the NO_x to N_2 .
14. A system for treating an exhaust gas comprising a catalyst article according to claim 11 and a source of reductant.
15. A method for regenerating a catalyst comprising:
 - contacting a catalyst composition according to any of claims 1 to 9 with an exhaust gas stream containing sulfur; and
 - regenerating the catalyst composition after the sulfur concentration on the catalyst is > 0.5 grams sulfur / liter of catalyst.



Application No: GB1602702.1

Examiner: Dr Peter Aspinall

Claims searched: 1-15

Date of search: 23 September 2016

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,Y	1-9 and 11-15	CN 103394369 B (UNIV TAIYUAN TECH) See EPODOC Abstract and WPI Abstract Accession Number 2014-B41154
X,Y	1, 2, 4, 6, 7, 9, 11 and 13-15	WO 2015/018815 A1 (BASF SE & TOKYO INST TECH) See in particular examples, page 36 lines 35-40.
X,Y	1, 2, 4, 6, 7, 9, 11 and 13-15	WO 2008/147546 A1 (SAUDI BASIC et al) See whole document, in particular pages 10-12.
X,Y	2 and 10	US 2014/161718 A1 (GM GLOBAL TECH) See examples and paragraph [0042]
X,Y	1, 2, 4, 6, 7, 9, and 11-15	Donny Gasah Synthesis and characterization of Cu/Ni-Zeolite-A for the direct conversion of methane to liquid hydrocarbon, Faculty of chemical and natural resources engineer, Universiti Malaysia Pahang, published May 2008

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

B01J

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

WPI, EPODOC



International Classification:

Subclass	Subgroup	Valid From
B01J	0029/76	01/01/2006
B01J	0029/56	01/01/2006
B01J	0029/90	01/01/2006
B01J	0035/00	01/01/2006
B01J	0037/02	01/01/2006