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(54) Title: HYDROTHERMALLY STABLE, LOW-TEMPERATURE NO_x REDUCTION NH_3 -SCR CATALYST

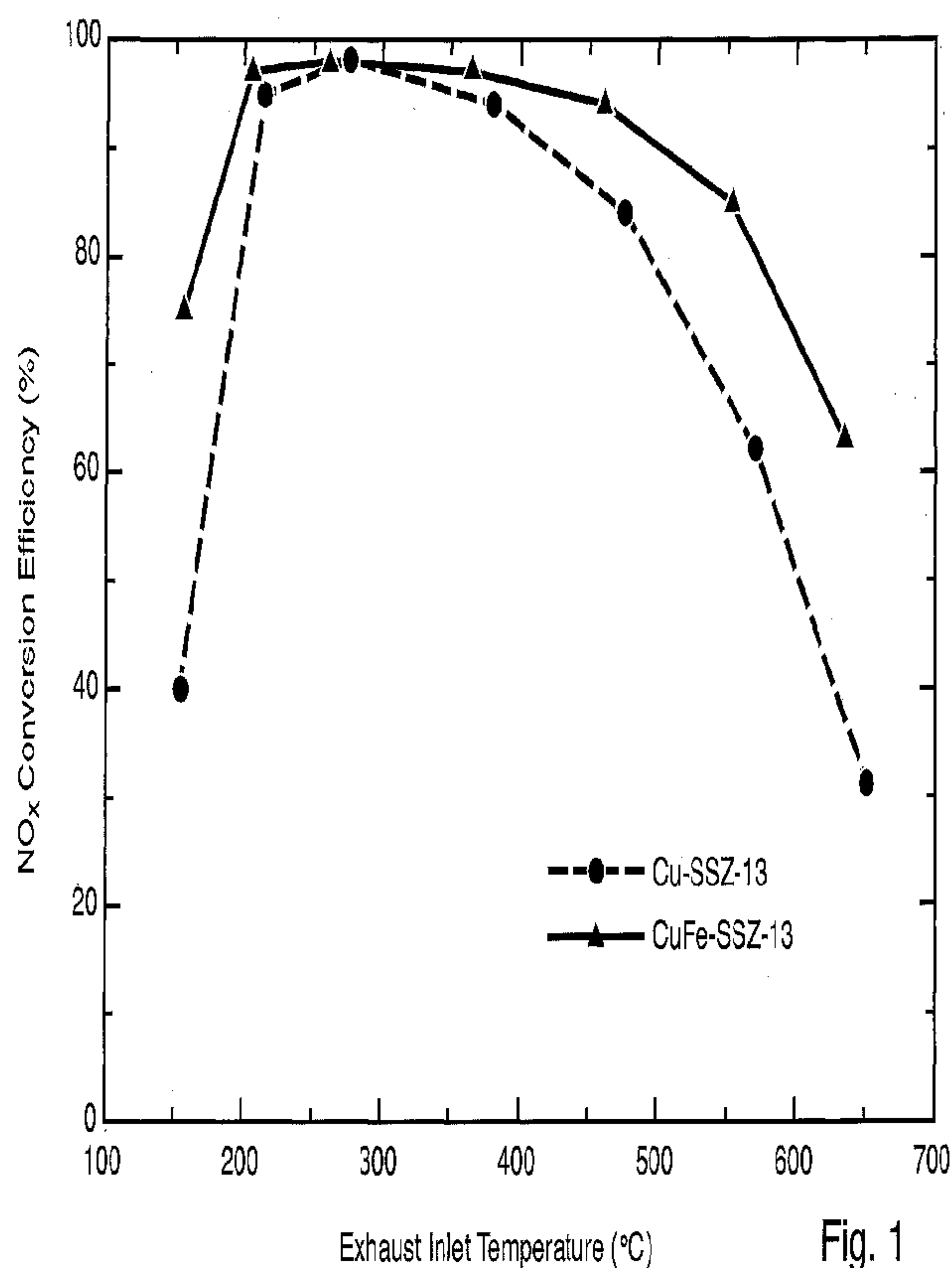


Fig. 1

(57) Abrégé/Abstract:

A catalyst composition includes a heterobimetallic zeolite characterized by a chabazite structure loaded with copper ions and at least one trivalent metal ion other than Al^{3+} . The catalyst composition decreases NO_x emissions in diesel exhaust and is suitable for operation in a catalytic converter.



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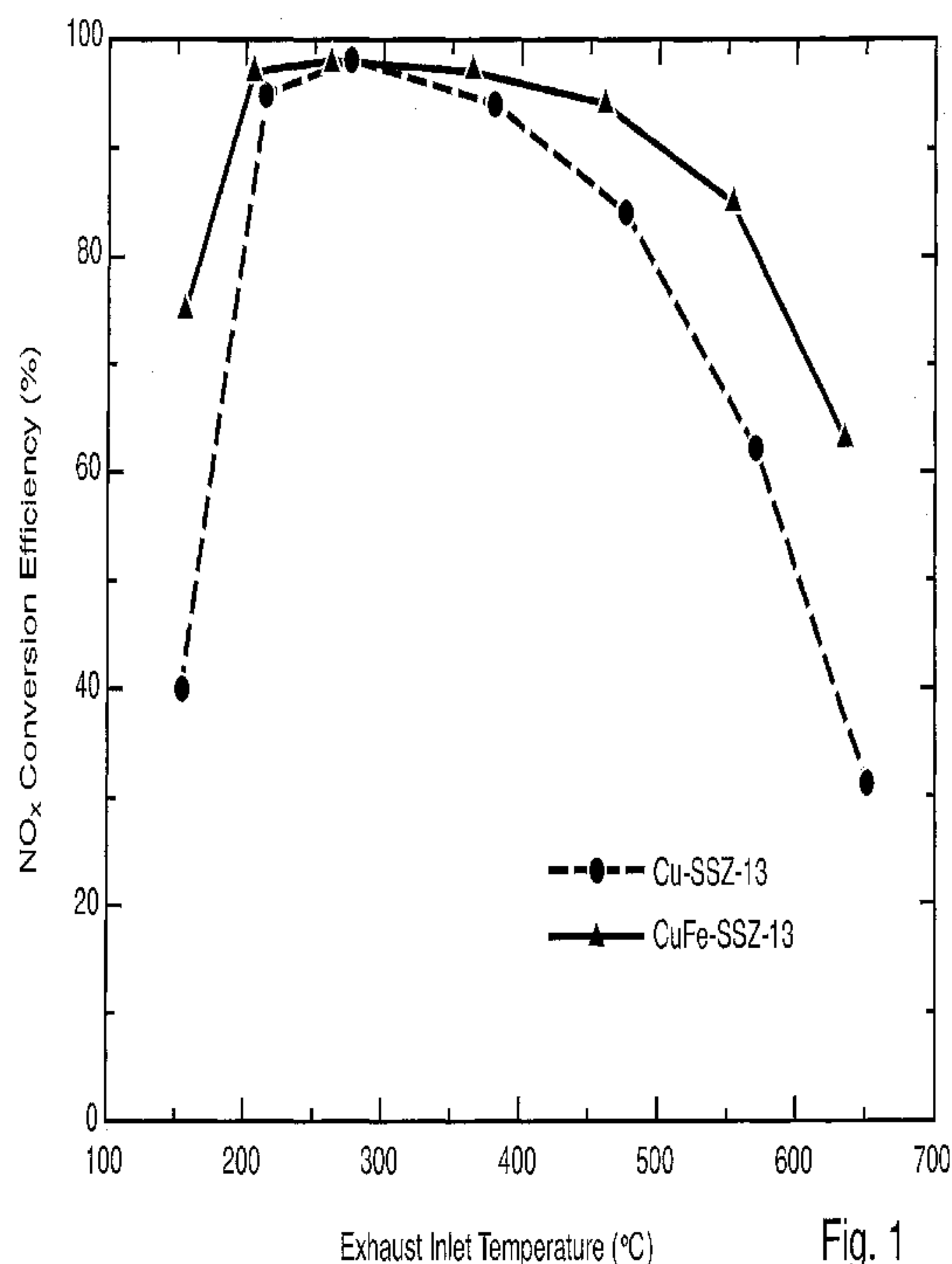
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Fig. 1

(57) Abstract: A catalyst composition includes a heterobimetallic zeolite characterized by a chabazite structure loaded with copper ions and at least one trivalent metal ion other than Al³⁺. The catalyst composition decreases NO_x emissions in diesel exhaust and is suitable for operation in a catalytic converter.

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HYDROTHERMALLY STABLE, LOW-TEMPERATURE NO_x REDUCTION NH₃-SCR CATALYST

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority from U.S. Application No. 13/404,071, filed on February 24, 2012, which is herein incorporated by reference in its entirety. Specifically referenced is U.S. Patent Application No. 12/855,794 filed on August 13, 2010, Publication No. 20120039759 published on February 16, 2012, entitled "Zeolite-Based SCR Catalysts and Their Use in Diesel Engine Emission Treatment" by Chaitanya K. Narula and Xiaofan Yang, the entire disclosure of which is incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] The United States Government has rights in this invention pursuant to contract no. DE-AC05-00OR22725 between the United States Department of Energy and UT-Battelle, LLC.

BACKGROUND OF THE INVENTION

[0003] Diesel engines are known to be significantly more fuel efficient than their gasoline counterparts. Therefore, the introduction of diesel engine in on-road and off-road systems (e.g., industrial or household equipment, such as heavy machinery and lawnmowers) is highly desirable. Furthermore, the gasoline engines, operating in oxygen rich environment (lean gasoline engines) are also more fuel efficient than currently used stoichiometric engines.

[0004] The high fuel efficiency of diesel engines and lean gasoline engines results in oxygen-rich (i.e., "lean") exhaust that primarily contains NO_x gases. Although NO_x gases can be efficiently removed from oxygen-poor exhausts, as produced in gasoline engine emissions, the removal of NO_x gases in diesel/lean gasoline engine lean emissions continues to be a significant challenge. In particular, the standard three-way catalyst

works well for gasoline engines but does not meet EPA regulatory requirements when used for diesel engines.

[0005] In order to meet EPA regulatory requirements for diesel engines, extensive efforts are under way to find catalysts that can effectively treat NO_x in the oxygen-rich emissions emitted by diesel engines. The leading approach for reduction of NO_x in diesel emissions is selective catalytic reduction (SCR). In SCR, ammonia or urea is often employed as a reductant. The best known NH₃-SCR catalysts for NO_x reduction under the lean environment of diesel engine emissions are Cu-ZSM-5 and Fe-ZSM-5. These have been shown to function effectively only within narrow temperature ranges. Cu-ZSM-5 generally exhibits a better NO_x reduction activity at lower temperatures while Fe-ZSM-5 exhibits better activity at higher temperatures. Thus, a combination of Cu-ZSM-5 and Fe-ZSM-5 zeolites (i.e., as a heterogeneous mixture) has been used in an effort to effectively treat NO_x within a broadened temperature range. The most recent generation NH₃-SCR catalyst is based on Cu-SSZ-13 and is now commercially available.

[0006] Although the Cu/Fe mixtures provide an improvement in emissions processing for diesel-operated passenger vehicles, the Cu/Fe mixtures is significantly inadequate at low temperatures. In particular, the catalysts currently employed do not efficiently reduce NO_x emissions at low temperatures, such as 150 – 200 °C, which is more critical in off-road diesel engines than in passenger vehicles. Moreover, the Cu/Fe mixture may be adequately efficient only within separate narrow temperature ranges, e.g., a high and a low temperature range. However, particularly for off-road diesel engines that can operate under a broad range of temperatures, there would be a significant benefit in a catalyst that can operate efficiently under a wide range of temperatures (for example, from 150 °C to 650 °C). If a gasoline engine is operated in lean mode, not much NO_x is produced at low temperature. However, the catalyst described in this invention is suitable for use with gasoline engines operating in lean mode as well as diesel engines used for transportation (cars, trucks, railroad engines, ships, etc.)

BRIEF SUMMARY OF THE INVENTION

[0007] In accordance with examples of the present invention, the foregoing and other objects are achieved by a catalyst composition that includes a heterobimetallic zeolite characterized by a chabazite structure loaded with copper ions and at least one trivalent metal ion other than Al^{3+} . The catalyst composition decreases NO_x emissions in diesel exhaust and is suitable for operation in a catalytic converter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Fig. 1 is a graph showing comparative performance of CuFe-SSZ-13 and Cu-SSZ-13 catalysts in accordance with examples of the present invention.

[0009] Fig. 2 is a graph showing comparative performance of CuFe-SSZ-13 and aged CuFe-SSZ-13 catalysts in accordance with examples of the present invention.

[0010] For a better understanding of the present invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims in connection with the above-described drawings.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The present invention is directed to a catalyst for mitigating (i.e., removing or reducing) NO_x emissions from hydrocarbon (for example, diesel, gasoline and/or kerosene exhaust). The catalyst includes a new class of heterobimetallic zeolites based on chabazite structure, such as CuFe-SSZ-13, for example. The new zeolites described herein overcome the hydrothermal durability issues of all known NH_3 -SCR catalysts for NO_x reduction while preserving their high NO_x reduction capability at low temperatures.

[0012] The zeolite considered herein can be any of the porous aluminosilicate structures known in the art that are stable under high temperature conditions, i.e., of at least 100 °C, 150 °C, 200 °C, 250 °C, 300 °C, and higher temperatures up to, for example, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, 750 °C, 800 °C, 850 °C, or 900 °C. In particular examples of the present invention, the zeolite is stable from at least 100 °C and up to 700 °C. Typically, the zeolite is ordered by having a crystalline or partly crystalline structure. The zeolite can generally be described as a three-dimensional framework

containing silicate (SiO_2 or SiO_4) and aluminate (Al_2O_3 or AlO_4) units that are interconnected (i.e., cross-linked) by the sharing of oxygen atoms.

[0013] The zeolite can be microporous (i.e., pore size of less than $2\ \mu\text{m}$), mesoporous (i.e., pore size within $2\text{-}50\ \mu\text{m}$, or sub-range therein), or a combination thereof. In several examples of the present invention, the zeolite material is completely or substantially microporous. By being completely or substantially microporous, the pore volume due to micropores can be, for example, 100%, or at least 95%, 96%, 97%, 98%, 99%, or 99.5%, with the remaining pore volume being due to mesopores, or in some examples of the present invention, macropores (pore size greater than $50\ \mu\text{m}$). In other examples of the present invention, the zeolite material is completely or substantially mesoporous. By being completely or substantially mesoporous, the pore volume due to mesopores can be, for example, 100%, or at least 95%, 96%, 97%, 98%, 99%, or 99.5%, with the remaining pore volume being due to micropores, or in some examples of the present invention, macropores. In yet other examples of the present invention, the zeolite material contains an abundance of both micropores and mesopores. By containing an abundance of both micropores and mesopores, the pore volume due to mesopores can be, for example, up to, at least, or precisely 50%, 60%, 70%, 80%, or 90%, with the pore volume balance being due to micropores, or vice-versa.

[0014] The various forms of zeolite are commonly known by respective abbreviations such as, for example, ABW, ACO, AEI, AEN, AFG, AFN, AFT, AFX, APC, APD, ATN, ATT, ATV, AWO, AWW, BCT, BIK, BOF, BRE, CAS, CDO, CHA, DFT, DOH, EAB, EPI, ERI, ESV, FAR, FRA, GIS, GIU, IHW, ITE, ITW, JBW, JRY, KFI, LAU, LEV, LIO, LOS, LTA, LTN, MAR, MON, MTF, MWW, NAT, NSI, OWE, PAU, PHI, RHO, RTE, RTH, RWR, SAS, SAT, SAV, SBN, SIV, SOD, STI, STT, THO, TOL, UEI, UFI, or ZON. Some particular examples of zeolites include the chabazite class of zeolites (for example, SSZ-13, SSZ-62, Phi, SAPO-34, LZ-218, and Linde D). The compositions, structures, and properties of chabazite zeolites are well-known in the art, and have been described in detail, as found in, for example, U.S. Patents 4,544,538, 6,709,644, 4,124,686, 4,333,859, and 2,950,952, the contents of which are incorporated herein by reference in their entirety.

[0015] The zeolite can have any suitable silica-to-alumina (i.e., $\text{SiO}_2/\text{Al}_2\text{O}_3$ or "Si/Al") ratio. For example, in various examples of the present invention, the zeolite can have a Si/Al ratio of precisely, at least, less than, or up to 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13,

14, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 120, 150, or 200, or a Si/Al ratio within a range bounded by any two of the foregoing values. In particular examples of the present invention, the zeolite possesses a Si/Al ratio of 1 to 45.

[0016] In particular examples of the present invention, the zeolite is SSZ-13, which belongs to the ABC-6 family of zeolites, all of which are also considered herein. In particular examples of the present invention, the SSZ-13 zeolite is represented by the formula $RN_aNa_bAl_{2.4}Si_{33.6}O_{72} \cdot wH_2O$ ($1.4 < a < 27$)($0.7 < b < 4.3$)($1 < w < 7$), where RN is N,N,N-1-trimethyladamantammonium.

[0017] Typically, the zeolite contains an amount of cationic species. As is well known in the art, the amount of cationic species is generally proportional to the amount of aluminum in the zeolite. This is because the replacement of silicon atoms with lower valent aluminum atoms necessitates the presence of countercations to establish a charge balance. Some examples of cationic species include hydrogen ions (H^+), alkali metal ions, alkaline earth metal ions, and main group metal ions. Some examples of alkali metal ions that may be included in the zeolite include lithium (Li^+), sodium (Na^+), potassium (K^+), rubidium (Rb^+), and cesium (Cs^+). Some examples of alkaline earth metal ions that may be included in the zeolite include (Be^{2+}), magnesium (Mg^{2+}), calcium (Ca^{2+}), strontium (Sr^{2+}), and barium (Ba^{2+}). Some examples of main group metal ions that may be included in the zeolite include boron (B^{3+}), gallium (Ga^{3+}), indium (In^{3+}), and arsenic (As^{3+}). In some examples of the present invention, a combination of cationic species is included. The cationic species can be in a trace amount (e.g., no more than 0.01 or 0.001%), or alternatively, in a significant amount (e.g., above 0.01%, and up to, for example, 0.1, 0.5, 1, 2, 3, 4, or 5% by weight of the zeolite).

[0018] The zeolite described above is loaded with an amount of copper ions. The copper ions can be cuprous (Cu^+) or cupric (Cu^{2+}) in nature. The copper loading can be any suitable amount. In different examples of the present invention, the copper loading is precisely, at least, less than, or up to, for example, 0.01%, 0.02%, 0.03%, 0.04%, 0.05%, 0.06%, 0.07%, 0.08%, 0.09%, 1.0%, 1.1%, 1.2%, 1.3%, 1.4%, 1.5%, 1.6%, 1.7%, 1.8%, 1.9%, 2.0%, 2.1%, 2.2%, 2.3%, 2.4%, or 2.5%, or a copper loading within a range bounded by any two of the foregoing values, wherein the loading is expressed as the amount of metal by weight of the zeolite. In particular examples of the present invention, the copper loading is any value up to 2.5%.

[0019] In addition to copper ions, the zeolite catalyst of the instant invention also includes at least one trivalent metal ion. As used herein, the term "trivalent metal ion" is defined as a trivalent metal ion other than aluminum (Al^{3+}). Without wishing to be bound by any theory, it is believed that the trivalent metal is incorporated into the zeolite material. Thus, the incorporated trivalent metal ion is believed to be bound in the zeolite to an appropriate number of oxygen atoms, i.e., as a metal oxide unit in close proximity (e.g., within electronic contact or communication) to the copper ions. The close proximity between the trivalent metal ions and copper ions is believed to cause a combined effect different than the cumulative effect of these ions when they are not in such close proximity. The effect primarily considered herein is the effect on the resulting catalyst's ability to process NO_x gases (i.e., the catalyst's NO_x conversion ability).

[0020] In some examples of the present invention, only one type of trivalent metal ion aside from aluminum is incorporated into the zeolite. In other examples of the present invention, at least two types of trivalent metal ions aside from aluminum are incorporated into the zeolite. In yet other examples of the present invention, at least three types of trivalent metal ions aside from aluminum are incorporated into the zeolite. In yet other examples of the present invention, precisely two or precisely three types of trivalent metal ions aside from aluminum are incorporated into the zeolite.

[0021] Each of the trivalent metal ions can be included in any suitable amount, such as, precisely, at least, less than, or up to, for example, 0.01%, 0.02%, 0.03%, 0.04%, 0.05%, 0.06%, 0.07%, 0.08%, 0.09%, 1.0%, 1.1%, 1.2%, 1.3%, 1.4%, 1.5%, 1.6%, 1.7%, 1.8%, 1.9%, 2.0%, 2.1%, 2.2%, 2.3%, 2.4%, or 2.5%, or an amount within a range bounded by any two of the foregoing values. In particular examples of the present invention, each of the trivalent metal ions can be included in an amount of, precisely, at least, less than, or up to 2.5%. In examples of the present invention where more than one type of trivalent metal ion is included, the loading of each metal can be independently selected from any of the above exemplary amounts or ranges therein. In other examples of the present invention, the total amount of trivalent metal ions other than aluminum conforms to any of the exemplary values provided above.

[0022] In a first set of examples of the present invention, at least one trivalent metal ion is selected from trivalent transition metal ions. The one or more transition metals can be selected from any or a select portion of the following types of transition metals: elements

of Groups IIIB (Sc group), IVB (Ti group), VB (V group), VIB (Cr group), VIIB (Mn group), VIIIB (Fe and Co groups) of the Periodic Table of the Elements. Some examples of trivalent transition metal ions include Sc^{3+} , Y^{3+} , V^{3+} , Nb^{3+} , Cr^{3+} , Fe^{3+} , and Co^{3+} . In other examples of the present invention, the trivalent metal ion excludes all transition metal ions, or alternatively, excludes any one, two, or more classes or specific examples of transition metal ions provided above. In particular examples of the present invention, the trivalent transition metal ions include Sc^{3+} , or Fe^{3+} , or a combination thereof.

[0023] In a second set of examples of the present invention, at least one trivalent metal ion is selected from trivalent main group metal ions. The one or more main group metals can be selected from any or a select portion of elements of Group IIIA (B group) and/or Group VA (N group) of the Periodic Table, other than aluminum. Some examples of trivalent main group metal ions include Ga^{3+} , In^{3+} , As^{3+} , Sb^{3+} , and Bi^{3+} . In other examples of the present invention, the trivalent metal ion excludes all main group metal ions other than aluminum, or alternatively, excludes any one, two, or more classes or specific examples of main group metal ions provided above. In particular examples of the present invention, the trivalent main group metal ions include at least In^{3+} .

[0024] In a third set of examples of the present invention, at least one trivalent metal ion is selected from trivalent lanthanide metal ions. Some examples of trivalent lanthanide metal ions considered herein include La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , and Lu^{3+} . In particular examples of the present invention, the trivalent lanthanide metal ion is selected from one or a combination of La^{3+} , Ce^{3+} , Pr^{3+} , and Nd^{3+} . In further particular examples of the present invention, the trivalent lanthanide metal ion is or includes La^{3+} .

[0025] In a fourth set of examples of the present invention, at least two trivalent metal ions are selected from trivalent transition metal ions. Some combinations of trivalent transition metal ions considered herein include Sc^{3+} in combination with one or more other trivalent transition metal ions, or Fe^{3+} in combination with one or more other trivalent transition metal ions, or Y^{3+} in combination with one or more other trivalent transition metal ions.

[0026] In a fifth set of examples of the present invention, at least two trivalent metal ions are selected from trivalent main group metal ions. Some combinations of trivalent main group metal ions considered herein include In^{3+} in combination with one or more other trivalent main group metal ions, or Ga^{3+} in combination with one or more other trivalent

main group metal ions, or As^{3+} in combination with one or more other trivalent main group metal ions.

[0027] In a sixth set of examples of the present invention, at least two trivalent metal ions are selected from trivalent lanthanide metal ions. Some combinations of trivalent lanthanide metal ions considered herein include La^{3+} in combination with one or more other trivalent lanthanide metal ions, or Ce^{3+} in combination with one or more other trivalent lanthanide metal ions, or Pr^{3+} in combination with one or more other trivalent lanthanide metal ions, or Nd^{3+} in combination with one or more other trivalent lanthanide metal ions.

[0028] In a seventh set of examples of the present invention, at least one trivalent metal ion is a trivalent transition metal ion and at least one trivalent metal ion is a trivalent lanthanide metal ion. For example, in particular examples of the present invention, at least one trivalent metal ion is selected from Sc^{3+} , Fe^{3+} , and/or Y^{3+} , and another trivalent metal ion is selected from La^{3+} , Ce^{3+} , Pr^{3+} , and/or Nd^{3+} .

[0029] In an eighth set of examples of the present invention, at least one trivalent metal ion is a trivalent transition metal ion and at least one trivalent metal ion is a trivalent main group metal ion. For example, in particular examples of the present invention, at least one trivalent metal ion is selected from Sc^{3+} , Fe^{3+} , and/or Y^{3+} , and another trivalent metal ion is selected from In^{3+} , Ga^{3+} , and/or In^{3+} .

[0030] In a ninth set of examples of the present invention, at least one trivalent metal ion is a trivalent main group metal ion and at least one trivalent metal ion is a trivalent lanthanide metal ion. For example, in particular examples of the present invention, at least one trivalent metal ion is selected from Sc^{3+} , Fe^{3+} , and/or Y^{3+} , and another trivalent metal ion is selected from La^{3+} , Ce^{3+} , Pr^{3+} , and/or Nd^{3+} .

[0031] In a tenth set of examples of the present invention, at least three trivalent metal ions are included in the zeolite. The at least three trivalent metal ions can be selected from trivalent transition metal ions, trivalent main group metal ions, and/or trivalent lanthanide metal ions.

[0032] In particular examples of the present invention, one, two, three, or more trivalent metal ions are selected from Sc^{3+} , Fe^{3+} , Y^{3+} , La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , In^{3+} , and/or Ga^{3+} . In more particular examples of the present invention, one, two, three, or more trivalent metal ions are selected from Sc^{3+} , Fe^{3+} , La^{3+} , and/or In^{3+} .

[0033] The zeolite catalyst described above is typically not coated with a metal-containing film or layer. However, the instant invention also contemplates the zeolite catalyst described above coated with a metal-containing film or layer as long as the film or layer does not substantially impede the catalyst from effectively functioning as a NO_x reduction catalyst as intended herein. By being coated, the film or layer resides on the surface of the zeolite. In some examples of the present invention, the surface of the zeolite refers to only the outer surface (i.e., as defined by the outer contour area of the zeolite catalyst), while in other examples of the present invention, the surface of the zeolite refers to or includes inner surfaces of the zeolite, such as the surfaces within pores or channels of the zeolite. The metal-containing film or layer can serve, for example, to adjust the physical characteristics of the catalyst, the catalytic efficiency, or catalytic selectivity. Some examples of metal-containing surfaces include the oxides and/or sulfides of the alkali metals, alkaline earth metals, divalent transition or main group metals (e.g., Zn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Pd²⁺, Pt²⁺, Sn²⁺, or Pb²⁺), tetravalent transition metals (e.g., Ti⁴⁺, Zr⁴⁺, Rh⁴⁺, Ir⁴⁺, Mn⁴⁺, Ge⁴⁺, Sn⁴⁺, and Te⁴⁺), pentavalent transition or main group metals (e.g., Nb⁵⁺, Ta⁵⁺, and Sb⁵⁺), and hexavalent transition metals (e.g., Cr⁶⁺, Mo⁶⁺, and W⁶⁺). In other examples of the present invention, one or more classes or specific types of any of the above additional metal ions are excluded from the zeolite catalyst.

[0034] The catalyst described herein can be synthesized by any suitable method known in the art. The method considered herein should incorporate the metal ions (i.e., copper and one or more trivalent metal ions) homogeneously into the zeolite. The resulting metal-loaded catalyst contains a homogeneous distribution of the metal ions on a molecular level, i.e., the catalyst does not contain macroscopic regions containing only one type of metal ion, as would be obtained by grinding and mixing of two zeolite sources that each contain a different metal ion.

[0035] In particular examples of the present invention, the catalyst described herein is prepared by, first, impregnating the zeolite with the metals to be loaded. The impregnating step can be achieved by, for example, treating the zeolite with one or more solutions containing the metals to be loaded. By treating the zeolite with the metal-containing solution, the metal-containing solution is contacted with the zeolite such that the solution is absorbed into the zeolite, preferably into the entire volume of the zeolite.

[0036] In one embodiment, the impregnating step is achieved by treating the zeolite with a solution that contains all of the metals to be loaded. In another embodiment, the impregnating step is achieved by treating the zeolite with two or more solutions, wherein the different solutions contain different metals or combinations of metals. Each treatment of the zeolite with an impregnating solution corresponds to a separate impregnating step. Typically, when more than one impregnating step is employed, a drying and/or thermal treatment step is employed between the impregnating steps.

[0037] The metal-impregnating solution contains at least one or more metal ions to be loaded into the zeolite, as well as a liquid carrier for distributing the metal ions into the zeolite. The metal ions are generally in the form of metal salts. Preferably, the metal salts are completely dissolved in the liquid carrier. The metal salt contains one or more metal ions in ionic association with one or more counteranions. Any one or more of the metal ions described above can serve as the metal ion portion. The counteranion can be selected from, for example, halides (F^- , Cl^- , Br^- , or I^-), carboxylates (e.g., formate, acetate, propionate, or butyrate), sulfate, nitrate, phosphate, chlorate, bromate, iodate, hydroxide, β -diketonate (e.g., acetylacetonate), and dicarboxylates (e.g., oxalate, malonate, or succinate). In some examples of the present invention, the counteranion may contain one or more metals, including one or more metals to be loaded into the zeolite. Some examples of such counter-anions include titanate, zirconate, vanadate, niobate, tantalate, chromate, molybdate, tungstate, arsenate, antimonate, stannate, and tellurate. In other examples of the present invention, one or more classes or specific types of any of the foregoing counter-anions are excluded from the impregnating solution (or alternatively, excluded from being incorporated into the zeolite).

[0038] In particular examples of the present invention, the catalyst is prepared by forming a slurry containing zeolite powder and the metals to be incorporated. The resulting slurry is dried and fired to form a powder. The powder is then combined with organic and/or inorganic binders and wet-mixed to form a paste. The resulting paste can be formed into any desired shape, e.g., by extrusion into rod, honeycomb, or pinwheel structures. The extruded structures are then dried and fired to form the final catalyst. In other examples of the present invention, the zeolite powder, metals, and binders are all combined together to form a paste, which is then extruded and fired.

[0039] After impregnating the zeolite, the metal-loaded zeolite is typically dried and/or subjected to a thermal treatment step (e.g., a firing or calcination step). The thermal

treatment step functions to permanently incorporate the impregnated metals into the zeolite, e.g., by forming metal-oxide bonds within the zeolite material. In different examples of the present invention, the thermal treatment step can be conducted at a temperature of at least 100 °C, 150 °C, 200 °C, 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, 750 °C, or 800 °C, or within a range therein, for a time period of, for example, 15 minutes, 30 minutes, 1 hour, 2 hours, 6 hours, 12 hours, 24 hours, 30 hours, 36 hours, or 48 hours, or within a range therein. In particular examples of the present invention, the thermal treatment step is conducted at a temperature of at least 500 °C for a time period of at least two hours. In some examples of the present invention, the thermal treatment step includes a temperature ramping step from a lower temperature to a higher temperature, and/or from a higher temperature to a lower temperature. For example, the thermal treatment step can include a ramp stage from 100 °C to 700 °C, or vice-versa, at a rate of 1, 2, 5, or 10 °C/min.

[0040] Generally, the one or more heat treatment steps are conducted under normal atmospheric pressure. However, in some examples of the present invention, an elevated pressure (e.g., above 1 atm and up to 2, 5, or 10 atm) is employed, while in other examples of the present invention, a reduced pressure (e.g., below 1, 0.5, or 0.2 atm) is employed. Furthermore, although the heat treatment steps are generally conducted under a normal air atmosphere, in some examples of the present invention, an elevated oxygen, reduced oxygen, or inert atmosphere is used. Some gases that can be included in the processing atmosphere include, for example, oxygen, nitrogen, helium, argon, carbon dioxide, and mixtures thereof.

[0041] Generally, the zeolite catalyst described herein is in the form of a powder. In a first set of examples of the present invention, at least a portion, or all, of the particles of the powder have a size less than a micron (i.e., nanosized particles). The nanosized particles can have a particle size of precisely, at least, up to, or less than, for example, 1, 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, or 950 nanometers (nm), or a particle size within a range bounded by any two of the foregoing values. In a second set of examples of the present invention, at least a portion, or all, of the particles of the powder have a size at or above 1 micron in size. The micron-sized particles can have a particle size of precisely, at least, up to, or less than, for example, 1, 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, or 100 microns (μm), or a particle size within a range bounded by any two of the foregoing

values. In some examples of the present invention, single crystals or grains of the catalyst correspond to any of the sizes provided above, while in other examples of the present invention, crystals or grains of the catalyst are agglomerated to provide agglomerated crystallites or grains having any of the above exemplary dimensions.

[0042] In other examples of the present invention, the zeolite catalyst can be in the form of a film, a coating, or a multiplicity of films or coatings. The thickness of the coatings or multiplicity of coatings can be, for example, 1, 2, 5, 10, 50, or 100 microns, or a range therein, or up to 100 micron thickness. In yet other examples of the present invention, the zeolite catalyst is in the form of a non-particulate (i.e., continuous) bulk solid. In still other examples of the present invention, the zeolite catalyst can be fibrous or in the form of a mesh.

[0043] The catalyst can also be mixed with or affixed onto a support material suitable for operation in a catalytic converter. The support material can be a powder (e.g., having any of the above particle sizes), granular (e.g., 0.5 mm or greater particle size), a bulk material, such as a honeycomb monolith of the flow-through type, a plate or multi-plate structure, or corrugated metal sheets. If a honeycomb structure is used, the honeycomb structure can contain any suitable density of cells. For example, the honeycomb structure can contain 100, 200, 300, 400, 500, 600, 700, 800, or 900 cells/in² (or from 62-140 cells/cm²) or greater. The support material is generally constructed of a refractory composition, such as those containing cordierite, mullite, alumina (e.g., α -, γ -, or θ -alumina), or zirconia, or a combination thereof. Honeycomb structures, in particular, are described in detail in, for example, U.S. Patents 5,314,665, 7,442,425, and 7,438,868, the contents of which are incorporated herein by reference in their entirety. When corrugated or other types of metal sheets are used, these can be layered on top of each other with catalyst material supported on the sheets such that passages remain that allow the flow of exhaust gas between the sheets. The layered sheets can also be formed into a structure, such as a cylinder, by winding the sheets.

[0044] The catalyst described herein preferably exhibits a NO_x conversion temperature profile that is improved over that of Cu-SSZ-13, as described in U.S. Patent 7,601,662.

[0045] In a first set of examples of the present invention, the catalyst described herein preferably exhibits a high NO_x conversion at 150 °C. As used herein, the phrase "high NO_x conversion at 150 °C" is defined as a NO_x conversion of at least or above 50%, 55%, 60%, 65%, 70%, 75%, 80%, or 85% at 150 °C.

[0046] In a second set of examples of the present invention, the catalyst described herein preferably exhibits a high NO_x conversion at 200 °C. As used herein, the phrase "high NO_x conversion at 200 °C" is defined as a NO_x conversion of at least or above 80%, 85%, or 90% at 200 °C.

[0047] In a third set of examples of the present invention, the catalyst described herein preferably exhibits a high NO_x conversion at a temperature in the range of 250 °C to 450 °C. As used herein, the phrase "high NO_x conversion at 250-450 °C " is defined as a NO_x conversion of at least or above 60%, 65%, 70%, 75%, 80%, 85%, or 90% at a temperature of 250 °C, 300 °C, 350 °C, 400 °C, or 450 °C, at a temperature in the range of 250 °C to 450 °C, or temperatures that vary within the range.

[0048] In a fourth set of examples of the present invention, the catalyst described herein preferably exhibits a high NO_x conversion at a temperature in the range of 500 °C to 525 °C. As used herein, the phrase "high NO_x conversion at 500-525 °C" is defined as a NO_x conversion of at least or above 60%, 65%, 70%, 75%, 80%, or 85% at a temperature in the range of 500 °C to 525 °C, or temperatures that vary within the range.

[0049] In a fifth set of examples of the present invention, the catalyst described herein preferably exhibits a high NO_x conversion at a temperature of 550° C. As used herein, the phrase "high NO_x conversion at 550° C" is defined as a NO_x conversion of at least or above 60%, 65%, 70%, 75%, or 80% at a temperature of 550° C.

[0050] In a sixth set of examples of the present invention, the catalyst described herein preferably exhibits a high NO_x conversion at a temperature in the range of 600 °C to 650 °C. As used herein, the phrase "high NO_x conversion at 600-650 °C" is defined as a NO_x conversion of at least or above 60%, 65%, 70%, 75%, or 80% at a temperature in the range of 600 °C to 650 °C, or temperatures that vary within the range.

[0051] In a seventh set of examples of the present invention, the catalyst described herein preferably exhibits a high NO_x conversion at 150 °C while also exhibiting a high NO_x conversion at 200°C, and/or a high NO_x conversion at 250-450°C, and/or a high NO_x conversion at 500-525°C, and/or a high NO_x conversion at 550°C, and/or a high NO_x conversion at 600-650°C.

[0052] In some examples, the invention is directed to a catalytic converter that contains therein as a catalyst the above-described metal-loaded zeolite catalyst. The catalyst is typically disposed on a refractory supporting element, such as corrugated metal sheets or a honeycomb structure, as described above. The catalytic converter can be any of the

catalytic converters known in the art, and particularly, those catalytic converters particularly suited for processing diesel fuel exhaust. The construction and operation of such catalytic converters are well known in the art, as described in detail in, for example, U.S. Patents 7,691,340, 7,678,348, 7,575,727, 7,442,425, 7,438,868, 7,412,824, 7,288,230, 6,919,052, and 5,314,665, the contents of which are all herein incorporated by reference in their entirety.

[0053] As basic elements, the catalytic converter typically contains the catalyst disposed on a supporting element such that passages are made available for exhaust to pass therethrough, and the supported catalyst enclosed in a metal casing. The metal casing is generally connected with one or more inlets (i.e., pipes) for transferring exhaust gases into the supported catalyst. The metal casing may also include one or more gaskets.

[0054] In particular examples of the present invention, the catalytic converter is connected with a source of ammonia in order for ammonia to mix in with the stream of exhaust gas. As is well known in the art, the ammonia functions as a reductant in selective catalytic reduction (SCR) processes. The ammonia can be in any suitable form, such as anhydrous ammonia, aqueous ammonia, urea, ammonium carbonate, ammonium formate, or ammonium carbamate. In some examples of the present invention, the ammonia source is supplied continuously into the exhaust stream before and/or during the time the exhaust stream reaches the catalyst. In other examples of the present invention, the ammonia is supplied intermittently. In other examples of the present invention, the ammonia source is supplied before the exhaust stream reaches the catalyst. In this way, the ammonia source is first absorbed into the catalyst before reacting with the exhaust stream. Generally, an ammonia storage tank is used to contain the ammonia source.

[0055] In designing a SCR system, numerous other elements can be interconnected with the catalytic converter and ammonia source. For example, a vaporizer can be included between the ammonia source and catalytic converter for converting (i.e., decomposing) the ammonia source into ammonia gas. A mixer may also be incorporated between the ammonia source and catalytic converter (or between vaporizer and catalytic converter) to mix ammonia with the exhaust stream. Other elements, such as heaters, pumps, and fans, can be included in order to optimize the system. The SCR system can be integrated into any system that makes use of a lean burn engine, particularly those engines that use diesel fuel. The SCR system can be integrated into, for example, the engine system of a

passenger vehicle, truck, utility boiler, industrial boiler, solid waste boiler (i.e., as used in the processing of municipal waste), ship, locomotive, tunnel boring machine, submarine, construction equipment, gas turbine, power plant, airplane, lawnmower, or chainsaw.

[0056] Examples have been set forth below for the purpose of illustration and to describe certain specific examples of the present invention of the invention. However, the scope of this invention is not to be in any way limited by the examples set forth herein.

EXAMPLE I

[0057] H-SSZ-13 was prepared according to U.S. Patent 4,544,538. Cu-SSZ-13 was synthesized as following: a 2.664 g sample of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ was dissolved in 600 mL de-ionized water (0.022M), followed by addition of H-SSZ-13 (10.00 g). The slurry was stirred for 2 hours at 50 °C. The blue-colored solid was collected by filtration after cooling, washed with de-ionized water, and calcined in air at 500 °C (10 °C/min) for 4 hours to afford Cu-SSZ-13. Elemental analysis: Cu 3.46, Al 4.05%.

[0058] CuFe-SSZ-13 was obtained by the following procedure: 10 g of Cu-SSZ-13 was suspended in a water solution of 50 mL 0.015M $\text{Fe}(\text{NO}_3)_3$, degassed with N_2 , and kept stirring for 2 hours at 80 °C. Yellow solid was obtained after filtration, and the filtrate was clear and colorless. The product was then calcined in air at 500 °C (2 °C/min) for 2 hours to yield pale yellow CuFe-SSZ-13. Elemental analysis: Cu 2.71%, Fe 0.357%, Al 3.86%.

[0059] CuFe-SSZ-13 can also be prepared by an incipient wetness method. In this method, 10 g of Cu-SSZ-13 was ground with 0.3 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and just enough water was added to cover the surface of Cu-SSZ-13. The color of Cu-SSZ-13 changed slowly from green to yellow. The sample was allowed to dry in air and then calcined in air at 500°C (2C/min) for 4 hours to yield pale yellow CuFe-SSZ-13.

EXAMPLE II

[0060] Cu-SSZ-13 and CuFe-SSZ-13 catalyst powders were comparatively tested. The catalyst powders were mixed with equal amounts (by weight) of inert cordierite and transferred to a bench-top reactor. A de-greening was done in a flow of 8.5% O_2 , 8% CO_2 , and 7.25% H_2O with balance N_2 at a temperature of 600 °C (inlet gas temperature)

and a space velocity of $50,000 \text{ h}^{-1}$ for two hours. NO_x conversion efficiency experiments employed simulated diesel exhaust containing 8.5% O_2 , 8% CO_2 , 7.25% H_2O , 250 ppm NO_2 , 250 ppm NO , 500 ppm NH_3 , and N_2 as balance at a space velocity of $50,000 \text{ h}^{-1}$ and evaluated in the temperature range of 150 °C to 650 °C. Results are shown in Fig. 1. CuFe-SSZ-13 catalyst clearly shows better performance in the 150-650 °C range. The NO_x conversion performance difference is especially noticeable at 150 °C where Cu-SSZ-13 converts ~40% NO_x whereas CuFe-SSZ-13 converts ~75% NO_x under test conditions.

EXAMPLE III

[0061] Accelerated aging was performed on the CuFe-SSZ-13 catalyst powder by employing an aging protocol that exposes catalyst to a temperature of 675 °C for 50 hours under a flow of air containing 10% water. Testing results are shown in Fig. 2.

[0062] CuFe-SSZ-13 catalyst demonstrates high hydrothermal durability and has high NO_x conversion performance in the 150-650 °C range. The NO_x reduction at 150 °C is ~65%, which is better than fresh Cu-SSZ-13, as shown in Fig. 1.

[0063] While there has been shown and described what are at present considered to be examples of the invention, it will be obvious to those skilled in the art that various changes and modifications can be prepared therein without departing from the scope of the inventions defined by the appended claims.

What is claimed is:

1. A catalyst composition comprising a heterobimetallic zeolite characterized by a chabazite structure loaded with copper ions and at least one trivalent metal ion other than Al^{3+} , and wherein said catalyst composition decreases NO_x emissions in diesel exhaust.
2. A catalyst in accordance with claim 1, wherein said at least one trivalent metal ion comprises a trivalent transition metal ion.
3. A catalyst in accordance with claim 2, wherein said at least one trivalent transition metal ion is selected from the group consisting of Sc^{3+} , Y^{3+} , V^{3+} , Nb^{3+} , Cr^{3+} , Fe^{3+} , and Co^{3+} .
4. A catalyst in accordance with claim 1, wherein said at least one trivalent metal ion comprises a trivalent main group metal ion.
5. A catalyst in accordance with claim 4, wherein said trivalent main group metal ion is selected from the group consisting of Ga^{3+} , In^{3+} , As^{3+} , Sb^{3+} , and Bi^{3+} .
6. A catalyst in accordance with claim 1, wherein said at least one trivalent metal ion is selected from the group consisting of Fe^{3+} , In^{3+} , Sc^{3+} , La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , and Lu^{3+} .
7. A catalyst in accordance with claim 1, wherein said at least one trivalent metal ion comprises a combination of at least two trivalent metal ions.
8. A catalyst in accordance with claim 7, wherein said at least two trivalent metal ions comprise trivalent transition metal ions.
9. A catalyst in accordance with claim 7, wherein at least one trivalent metal ion comprises a trivalent transition metal ion and wherein at least one other trivalent metal ion comprises a trivalent lanthanide metal ion.
10. A catalyst in accordance with claim 7, wherein at least one trivalent metal ion comprises a trivalent transition metal ion and wherein at least one other trivalent metal ion comprises a trivalent main group metal ion.

11. A catalyst in accordance with claim 7, wherein at least one trivalent metal ion comprises a trivalent main group metal ion and wherein at least one other trivalent metal ion comprises a trivalent lanthanide metal ion.
12. A catalyst in accordance with claim 1, wherein said zeolite comprises CuFe-SSZ-13.
13. A catalyst in accordance with claim 1, wherein said catalyst exhibits a NO_x conversion at 150 °C of at least 60%.
14. A catalyst in accordance with claim 13, wherein said catalyst also exhibits a NO_x conversion at 200 °C of at least 85%.
15. A catalyst in accordance with claim 13, wherein said catalyst also exhibits a NO_x conversion at 600 °C of at least 65%.
16. A catalytic converter comprising a catalyst loaded onto a refractory substrate, said catalyst comprising a heterobimetallic zeolite characterized by a chabazite structure loaded with copper ions and at least one trivalent metal ion other than Al³⁺, and wherein said catalyst decreases NO_x emissions in diesel exhaust.
17. A catalytic converter in accordance with claim 16, wherein said at least one trivalent metal ion comprises a trivalent transition metal ion.
18. A catalytic converter in accordance with claim 17, wherein said trivalent transition metal ion is selected from the group consisting of Sc³⁺, Y³⁺, V³⁺, Nb³⁺, Cr³⁺, Fe³⁺, and Co³⁺.
19. A catalytic converter in accordance with claim 16, wherein said at least one trivalent metal ion comprises a trivalent main group metal ion.
20. A catalytic converter in accordance with claim 19, wherein said trivalent main group metal ion is selected from the group consisting of Ga³⁺, In³⁺, As³⁺, Sb³⁺, and Bi³⁺.
21. A catalytic converter in accordance with claim 16, wherein said at least one trivalent metal ion is selected from the group consisting of Fe³⁺, In³⁺, Sc³⁺, La³⁺, Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, and Lu³⁺.

22. A catalytic converter in accordance with claim 16, wherein said at least one trivalent metal ion comprises a combination of at least two trivalent metal ions.
23. A catalytic converter in accordance with claim 22, wherein said at least two trivalent metal ions comprise trivalent transition metal ions.
24. A catalytic converter in accordance with claim 22, wherein at least one trivalent metal ion comprises a trivalent transition metal ion and wherein at least one other trivalent metal ion comprises a trivalent lanthanide metal ion.
25. A catalytic converter in accordance with claim 22, wherein at least one trivalent metal ion comprises a trivalent transition metal ion and wherein at least one other trivalent metal ion comprises a trivalent main group metal ion.
26. A catalytic converter in accordance with claim 22, wherein at least one trivalent metal ion comprises a trivalent main group metal ion and wherein at least one other trivalent metal ion comprises a trivalent lanthanide metal ion.
27. A catalytic converter in accordance with claim 16, wherein said zeolite comprises CuFe-SSZ-13.
28. A catalytic converter in accordance with claim 16, wherein said catalyst exhibits a NO_x conversion at 150 °C of at least 60%.
29. A catalytic converter in accordance with claim 28, wherein said catalyst exhibits a NO_x conversion at 200 °C of at least 85%.
30. A catalytic converter in accordance with claim 28, wherein said catalyst exhibits a NO_x conversion at 600 °C of at least 65%.
31. A catalytic converter in accordance with claim 16, wherein said refractory substrate is characterized by a structure selected from the group consisting of a rod structure, a honeycomb structure, and a pinwheel structure.

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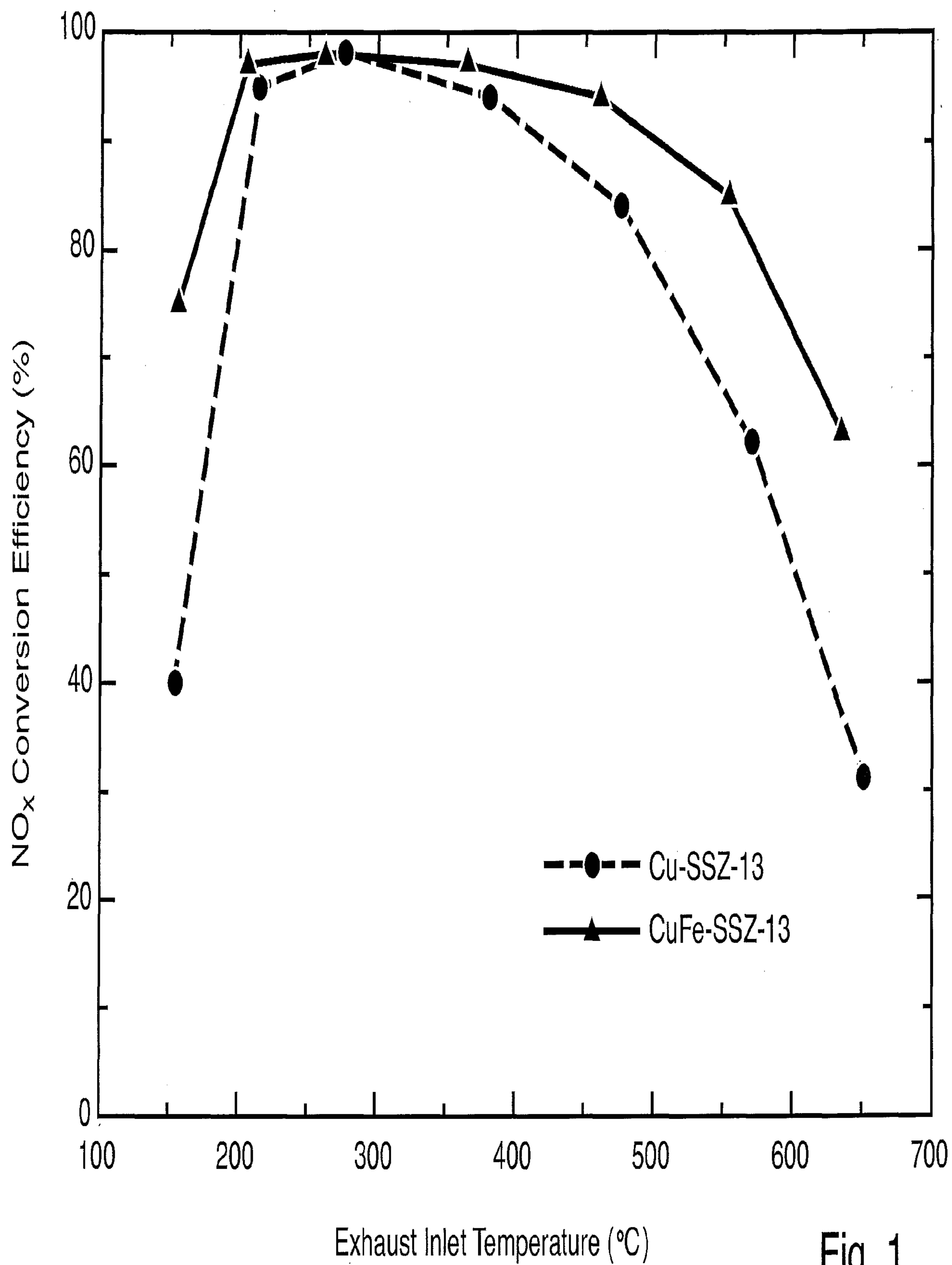


Fig. 1

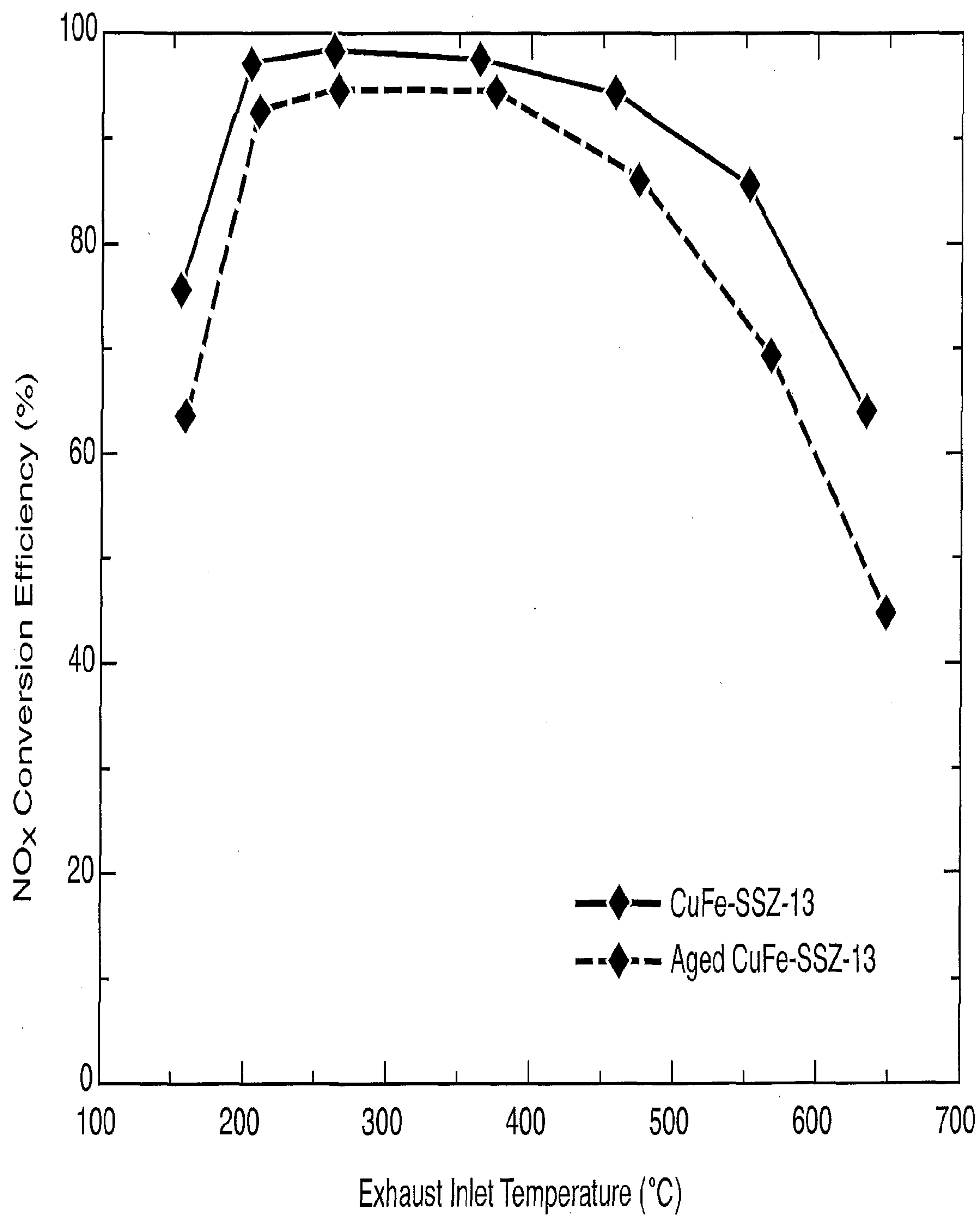


Fig. 2

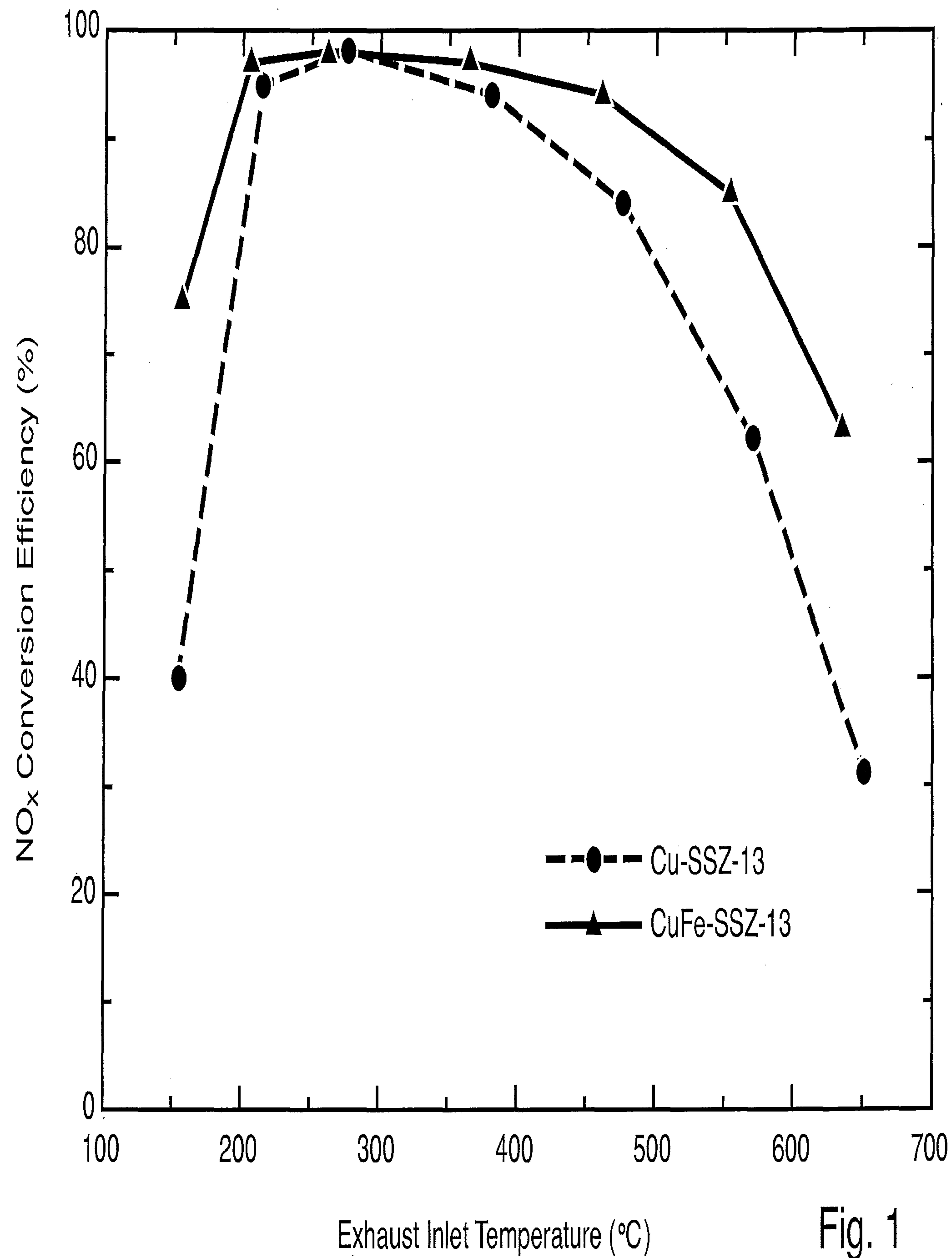


Fig. 1