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(54) **NOVEL CATALYST FOR SELECTIVE NOX  
REDUCTION USING HYDROCARBONS**

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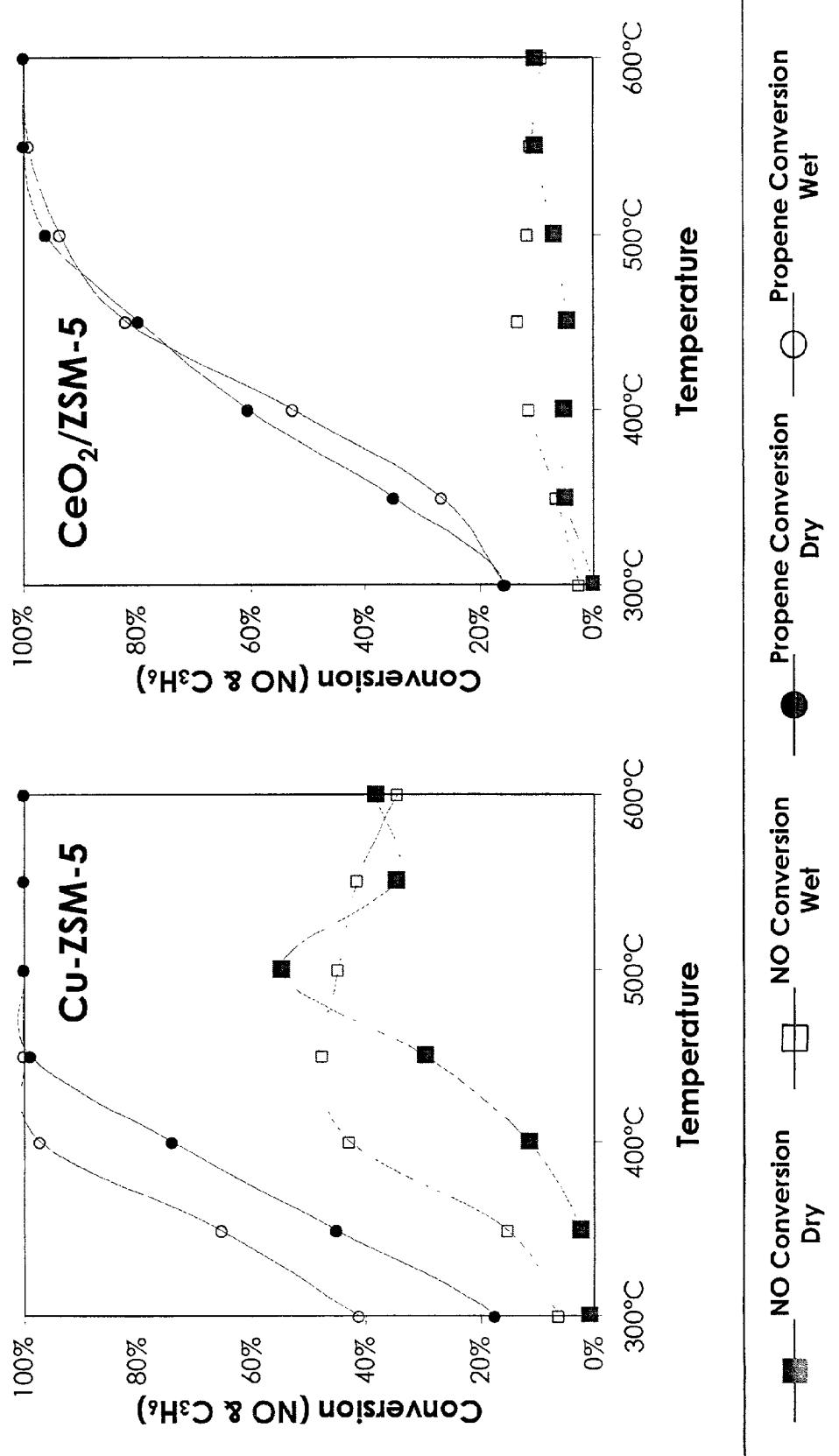
(57) **ABSTRACT**

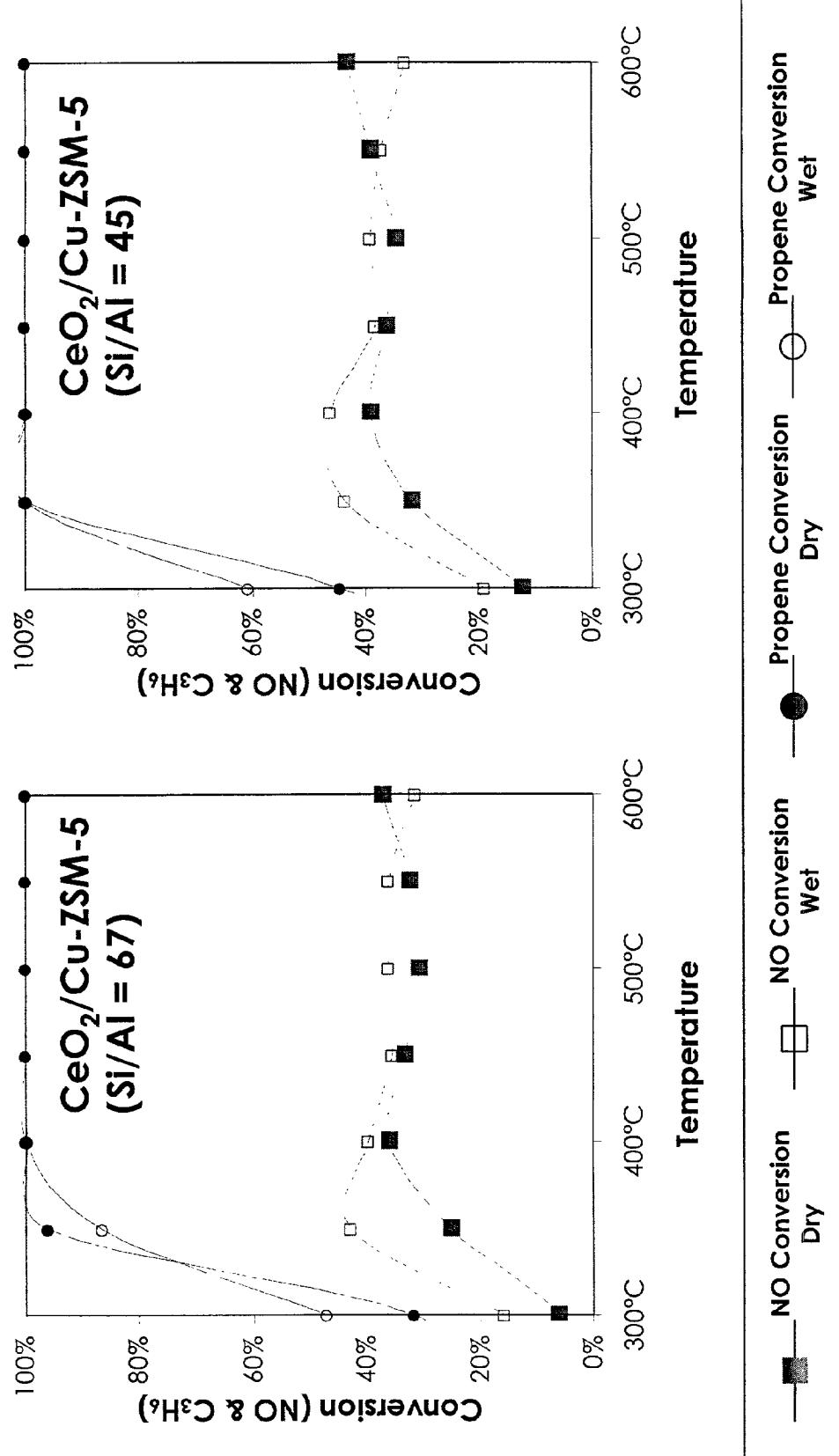
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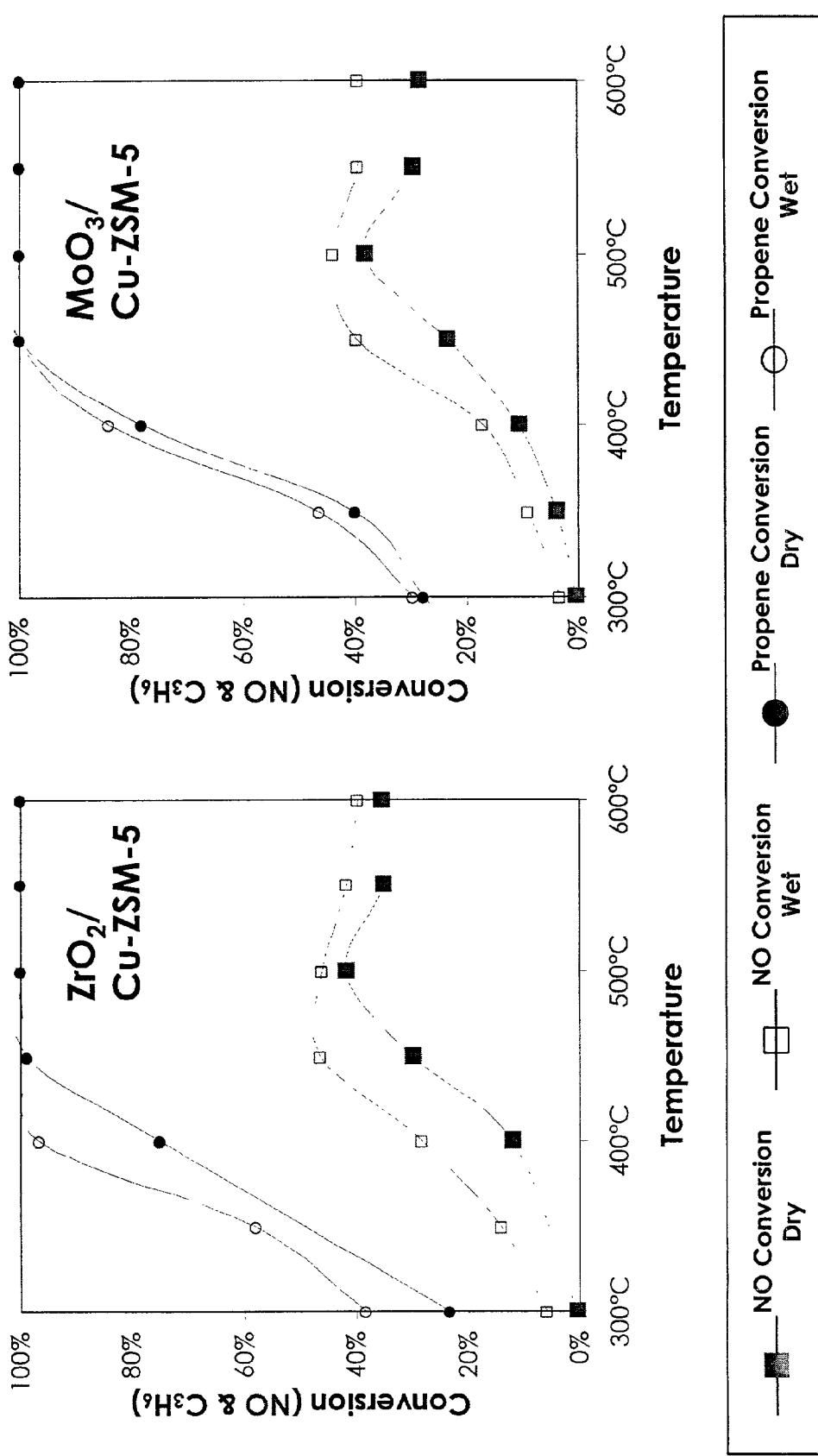
This invention discloses a catalyst and process for removing nitrogen oxides from exhaust streams under lean burn conditions using hydrocarbons as the reductant. Catalysts consists of two phases, a metal exchanged molecular sieve and a stabilizing metal oxide associated with the molecular sieve.

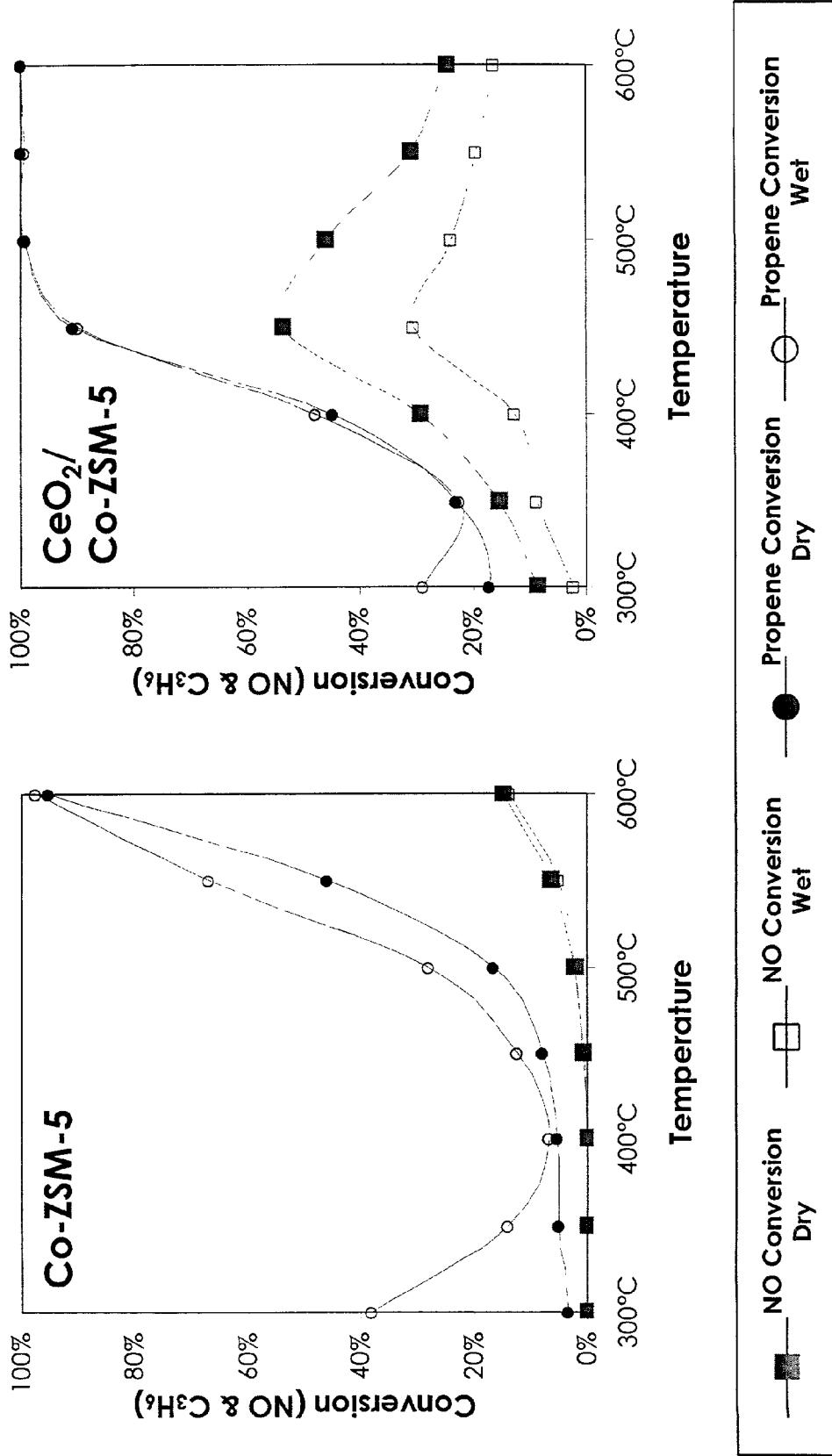
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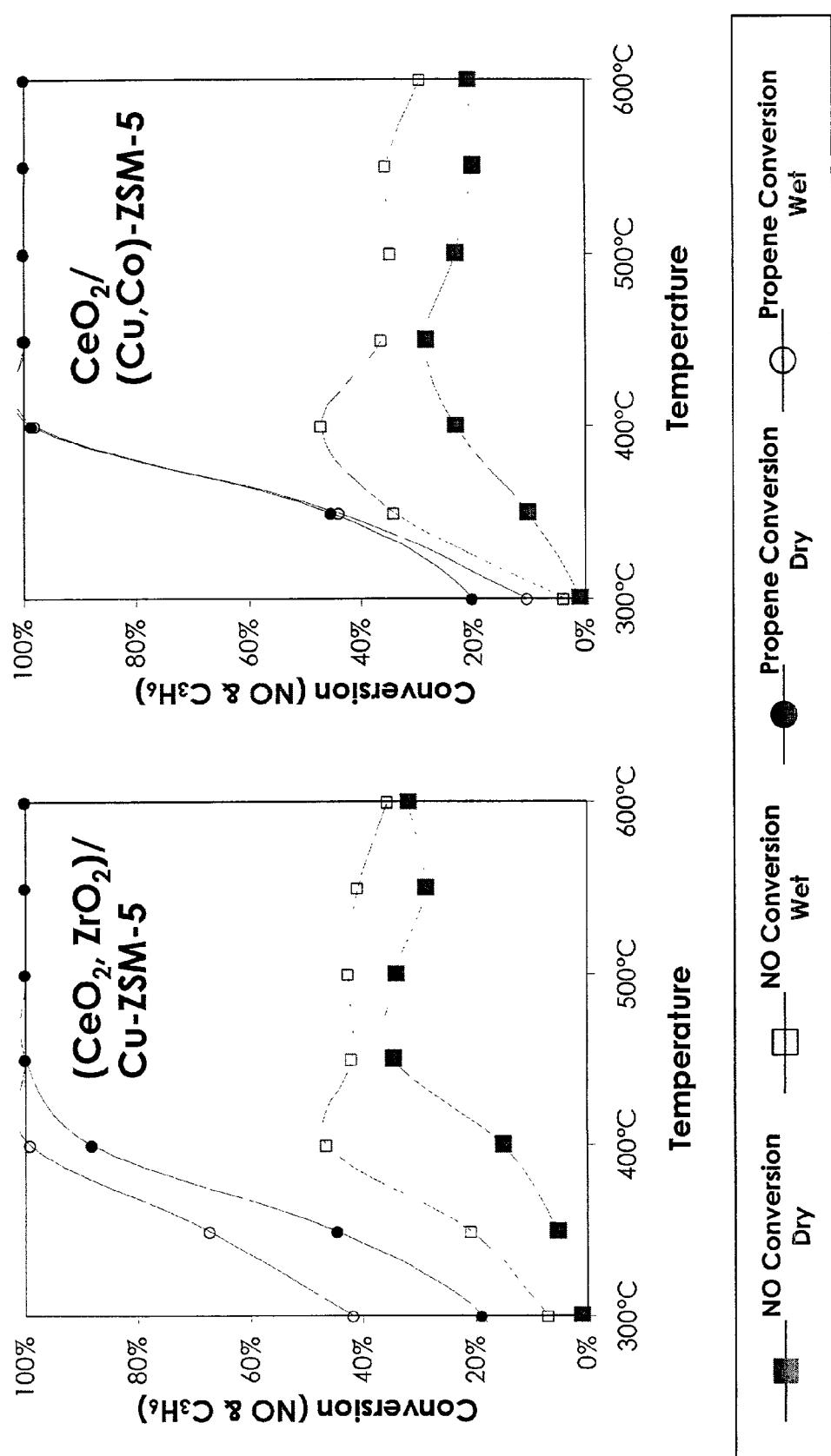
**Figure 1**

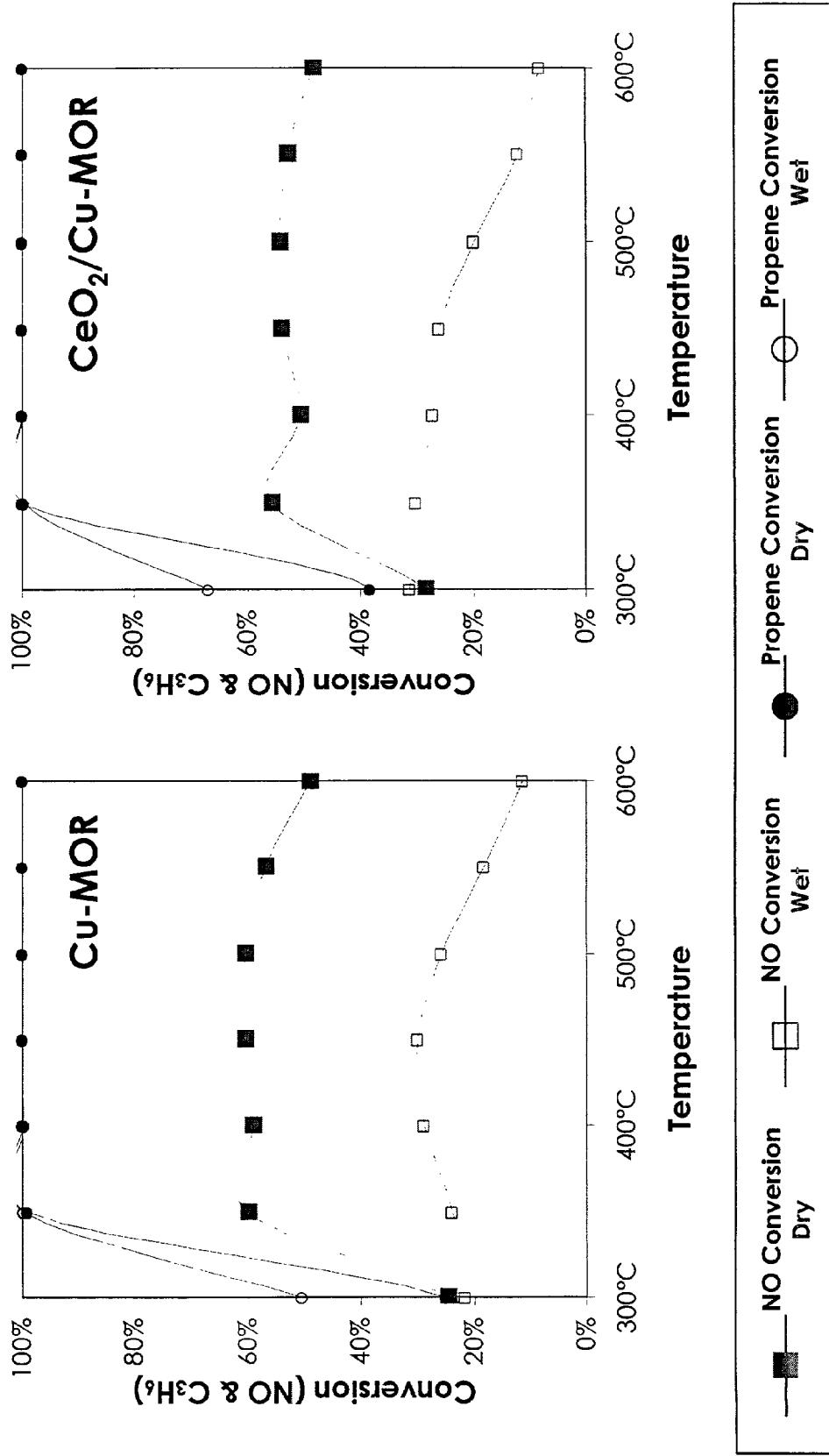


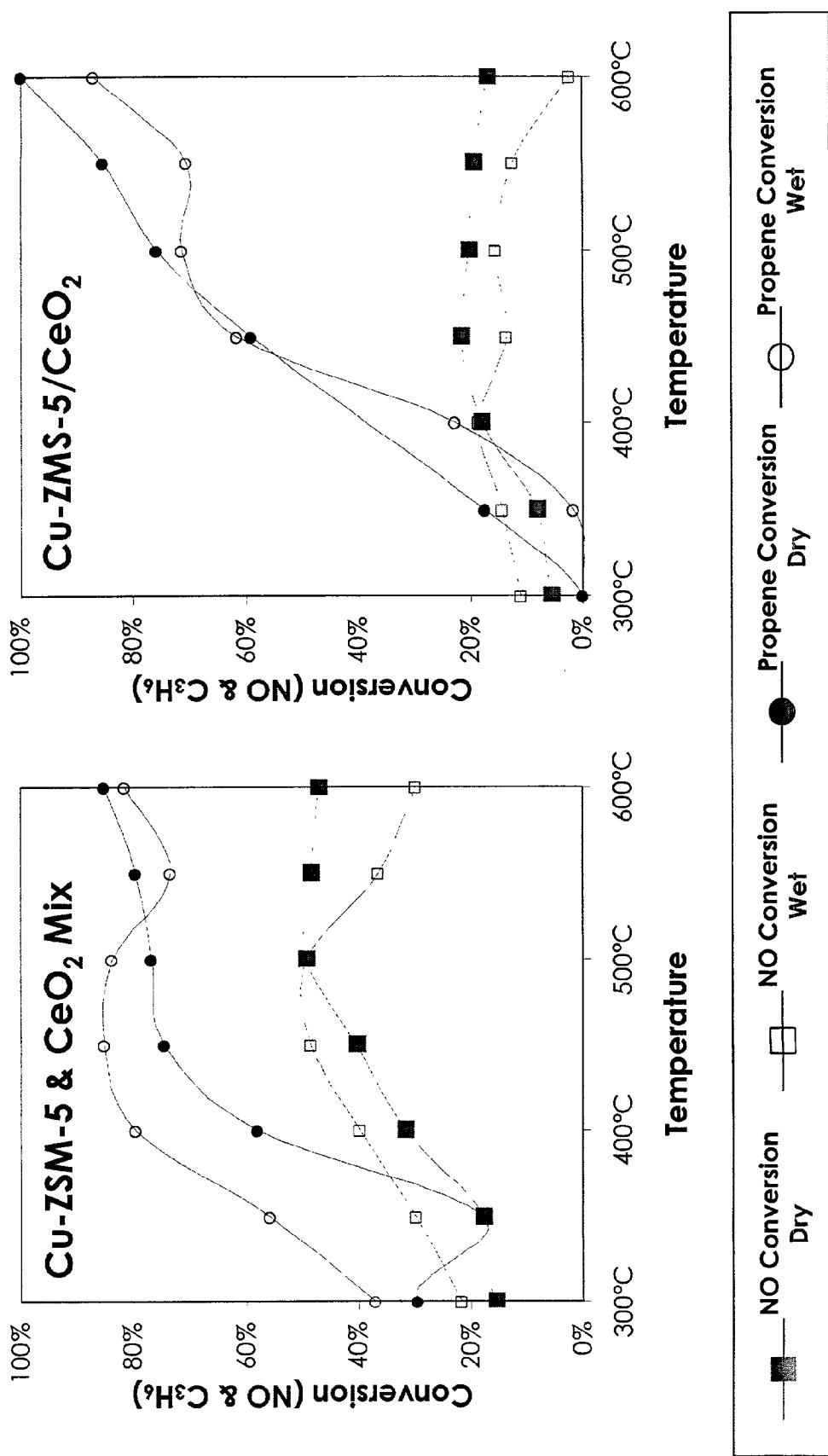
**Figure 2**

**Figure 3**

**Figure 4**

**Figure 5**

**Figure 6**

**Figure 7**

## NOVEL CATALYST FOR SELECTIVE NO<sub>x</sub> REDUCTION USING HYDROCARBONS

### CONTRACTUAL ORIGIN OF THE INVENTION

[0001] The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the U.S. Department of Energy (DOE) and The University of Chicago representing Argonne National Laboratory.

### FIELD OF THE INVENTION

[0002] The present invention relates to the reduction of nitrogen oxides (NO<sub>x</sub>) present in a lean burn exhaust by the selective catalyst reduction of NO<sub>x</sub> by a hydrocarbon with a bifunctional catalyst.

### BACKGROUND OF THE INVENTION

[0003] The combustion of fossil fuels unavoidably leads to the formation of nitrogen oxides (NO<sub>x</sub>), which if released to the atmosphere, can lead to acid rain and detrimental interactions with ozone. Increasing government regulations around the world have called for continued NO<sub>x</sub> emission reductions from both stationary and mobile sources, requiring new and improved technologies that can remove NO<sub>x</sub> from exhaust streams. While three-way catalysts have been optimized to reduce NO<sub>x</sub> emissions in rich-burn exhaust as from consumer automobiles, these catalysts are ineffective under lean-burn conditions, as usually observed with stationary sources or diesel engines. Reduction of NO<sub>x</sub> with ammonia has been used industrially for stationary sources. However, it is less desirable (especially in transportation systems) due to the toxic nature of the ammonia which must be stored locally. Alternative catalytic processes have been investigated for operation under lean burn conditions, with the selective catalytic reduction (SCR) of NO<sub>x</sub> with hydrocarbons being one of the most promising. These hydrocarbons are more readily available and pose less of a emission problem.

[0004] A large number of materials have been found to be catalytically active for SCR. By far, the most investigated are metal-exchanged zeolites, such as Cu-ZSM-5, Co-ZSM-5, and Fe-ZSM-5. These have been found to be very active for SCR using C<sub>3</sub> hydrocarbons, with Cu-ZSM-5 being the most active. However, the zeolite-based materials lose much of their activity when water (common in exhaust streams) is added to the exhaust stream. The exact effects of water are not well known; it is speculated that either dealumination of the zeolite framework occurs which reduces the number of active sites, or that the metal sites agglomerate or are over-oxidized and lose their activity. While other catalysts that possess greater water stability have been found, such as metal-supported oxides, these tend to lack the desired activity seen by the metal zeolites, and produce large amounts of N<sub>2</sub>O (also a major pollutant).

### SUMMARY OF THE INVENTION

[0005] The present invention is the development of bifunctional catalysts that combine active metal-exchanged zeolite phases along with metal oxide stabilizing phases that offer hydrothermal stability with sustained activity at low temperature for lean burn exhaust under SCR conditions.

[0006] Accordingly, it is a principal object of this invention to provide an effective method and catalyst for the reaction of NO<sub>x</sub> in lean burn exhaust having water present.

[0007] Another object of the invention is to provide a two part catalyst comprising a zeolite supported transition metal and a stabilizing oxide.

[0008] Still another object of this invention is to provide a method of remediating the concentration of nitrogen oxides (NO<sub>x</sub>) in the exhaust from lean burn combustion in the presence of water in which the exhaust containing water and NO<sub>x</sub> is contacted with one or more of an alkane or alkene reductant or mixtures thereof at a temperature of not greater than about 600° C. with a two-part catalyst including a molecular sieve supported transition metal and a stabilizing metal oxide.

[0009] The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0010] For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

[0011] FIG. 1 is a graphical representation of the conversion of NO<sub>x</sub> and propene as a function of temperature for a Cu-ZSM-5 catalyst and a CeO<sub>2</sub>/ZSM-5 catalyst. Closed symbols represent conversions under dry conditions, while open symbols represent conversions under wet (10% water) conditions;

[0012] FIG. 2 is a graphical representation of the conversion of NO<sub>x</sub> and propene zeolite supported copper catalysts stabilized with ceria illustrating various silicon to aluminum ratios;

[0013] FIG. 3 is a graphical representation of the conversion of NO<sub>x</sub> and propene as a function of temperature for copper supported zeolite stabilized with ZrO<sub>2</sub> and a copper supported zeolite stabilized with molybdenum oxide;

[0014] FIG. 4 is a graphical representation of the conversion of NO<sub>x</sub> and propene as a function of temperature for a cobalt supported zeolite and a cobalt supported zeolite stabilized with CeO<sub>2</sub>;

[0015] FIG. 5 is a graphical representation of the conversion of NO<sub>x</sub> and propene as a function of temperature for copper supported zeolite stabilized with CeO<sub>2</sub> and ZrO<sub>2</sub> and a copper and cobalt supported zeolite;

[0016] FIG. 6 is a graphical representation of the conversion of NO<sub>x</sub> and propene as a function of temperature for a copper supported mordenite and a copper supported mordenite stabilized with CeO<sub>2</sub>; and

[0017] FIG. 7 is a graphical representation of the conversion of NO<sub>x</sub> and propene as a function of temperature for a physical mixture of Cu-ZSM-5 and CeO<sub>2</sub> and Cu-ZSM-5/CeO<sub>2</sub>.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

[0018] While the preferred embodiment is generally illustrated by reference to examples involving a catalyst composed of a zeolite supported copper metal impregnated with a ceria stabilizing oxide, it should be understood that a variety of molecular sieve materials are satisfactory including zeolites. Specifically, only zeolite Y, zeolite beta, mordenite, ferrierite, ZSM-5, and ZSM-12 have been used. The molecular sieve should have a pore size of at least about 4 Å. Moreover, any transition metal would be adequate to be supported by a molecular sieve in a wide variety of concentrations. However, commonly used transition metals are copper, cobalt, iron, molybdenum, vanadium and various combinations thereof. Also, the supporting oxides can be any one or more of the rare earth oxides (such as cerium oxide) and transition metal oxides (such as zirconium oxide, molybdenum oxide, vanadium oxide and niobium oxide).

[0019] Specifically, a wide variety of pore size zeolites has been investigated and it is preferred that the pore size in the range of from about 4 Å and up to about 8 Å. In the art, these are referred to as medium pore and wide pore zeolites. Investigations have been conducted using various water concentrations up to about 20%. It is believed that the stabilizing oxide may be present in the catalyst in the range of from about 0.1% by weight to about 5% by weight including the molecular sieve. It is also believed that the typical exchange levels for the transition metal may be anywhere from about 25-100%. Moreover, a variety of ratios of silicon to aluminum have been tested in zeolites and found to be satisfactory. Silicon to aluminum ratios found to be satisfactory are generally between about 238 and about 17 to one. While the reductions herein use propene ( $C_3H_6$ ) any alkane or alkene between  $C_1$  and  $C_{16}$  is acceptable.

[0020] Most of the examples investigated have been using the Cu-ZSM-5 and CeO<sub>2</sub> system. Besides physically mixing these catalysts, the bifunctional catalysts were synthesized in two distinct ways to vary the way the phases were mixed. The methods used here can be easily extended to incorporate a number of oxides, such as the rare earth oxides, zirconium oxide, vanadium oxide, the molybdenum oxides, the niobium oxides or combinations thereof, onto any transition metal-exchanged zeolite, including but not limited to Co-ZSM-5, Fe-ZSM-5, or Cu-ZSM-5 as well as the multimetallic-exchanged zeolites. Furthermore, it is believed that other zeolites besides ZSM-5, such as zeolite Y, Beta zeolite, the others synthetic or natural zeolites, or other molecular-sieve-like materials, such as silica-aluminophosphate (SAPO) or MCM-41, could be used as the primary component of the metal support.

[0021] CeO<sub>2</sub>/Cu-ZSM-5: Copper was ion exchanged with a ZSM-5 zeolite via typical means. A 0.01 M solution of Cu(NO<sub>3</sub>)<sub>2</sub> was prepared, and 2 g of H-ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=80) was stirred into 40 ml of the solution. The slurry was stirred overnight at room temperature, then filtered, washed with distilled water, dried at 100° C. in a vacuum oven, then calcined in air at 500° C. for 3 hrs. Copper loadings can be adjusted by changing the concentration of the solution, the pH of mixing, or by repeated exchanges with the solution. Ceria was introduced by first diluting a ceria sol from 20 wt % to 0.01M. Two grams of the Cu-ZSM-5 was mixed with 40 ml of the ceria solution, and was stirred overnight at room

temperature. The slurry was filtered, washed, dried, and then calcined using the same conditions above. This catalyst will be referred to as "CeO<sub>2</sub>/Cu-ZSM-5".

[0022] Cu-ZSM-5/CeO<sub>2</sub>: High surface area ceria was first prepared following traditional procedures. Five grams of cerium carbonate was slowly mixed with 4.5 ml of glacial acetic acid to produce cerium acetate. The sample was dried in a vacuum over at 100° C., the calcined in air at 425° C. to produce cerium oxide. The ceria was coated with a layer of Al<sub>2</sub>O<sub>3</sub> to act as a template by mixing 2 g of the ceria with 40 ml of a 0.01M Al<sub>2</sub>O<sub>3</sub> sol (diluted from a 20 wt % sol), stirring overnight, then filtering, washing, drying, and calcining in air at 500° C. as above. The zeolite precursor solution was prepared by mixing a solution containing NaOH, dissolved Al foil, and H<sub>2</sub>O with tetraethylorthosilicate (TEOS) and tetrapropylammonium hydroxide (TPAOH) such that the molar concentrations in the final solution was 4:0.06:571:6:1 NaOH:Al:H<sub>2</sub>O:TEOS:TPAOH. The solution was stirred at room temperature overnight, then approximately 40 ml was added to 2 g of the Al<sub>2</sub>O<sub>3</sub> coated ceria in an autoclave. The autoclave was heated to 175° C. for 6 hrs under autogenous pressure. After rapid cooling, the sample was filtered, washed, dried, then calcined for 6 hrs in air at 500° C. to remove residual organic compounds. Copper was exchanged with the zeolite film/ceria following the methods listed above for CeO<sub>2</sub>/Cu-ZSM-5. The final catalyst will be referred to as "Cu-ZSM-5/CeO<sub>2</sub>".

[0023] In addition to the catalysts above, additional catalysts tested included: a Cu-ZSM-5 prepared similarly to CeO<sub>2</sub>/Cu-ZSM-5 but without ceria addition, and a quantity of the Cu-ZSM-5 catalyst mixed in a equal weight ratio with the high surface area ceria prepared above. This latter catalyst was mixed by gentle grinding in a mortar for about 10 minutes.

[0024] The NO<sub>x</sub> conversion activity was performed as follows. Approximately 150 mg of sample was loaded into a quartz tube, and connected to a gas manifold system. Prior to reaction, the sample was pretreated in He at 500° C. for one hour. Gases were available as 5.025% NO in He, 3.0% C<sub>3</sub>H<sub>6</sub> in He, 4.96% O<sub>2</sub> in He, and pure He. The gases were controlled with Brooks 5850e mass flow controllers as to introduce a gas flow of 1000 ppm NO, 1000 ppm C<sub>3</sub>H<sub>6</sub>, 2% O<sub>2</sub>, and the balance He at a space velocity of approximately 30,000 hr<sup>-1</sup>. For water tests, water was pumped into the system with a syringe pump and the water and gas flows were adjusted to give the same concentration of gases above and 10% H<sub>2</sub>O. The reaction was allowed to proceed at 500° C. for 3 hrs prior to taking any readings. The reaction temperature was varied between 200 and 600° C. in 50° C. increments, allowing for at least 30 minutes at temperature before analyzing the effluent. The reaction effluent was analyzed using an MTI micro gas chromatograph with molecular sieve 5A and poropak Q columns for the stationary and hydrocarbon gases, or with a California Analytical Instruments NO<sub>x</sub> detector, model HCLD-400, for the NO and NO<sub>2</sub>.

[0025] The reduction of NO<sub>x</sub> and C<sub>3</sub>H<sub>6</sub> over Cu-ZSM-5 and ceria on ZSM-5 are shown on FIG. 1. As can be seen, at about 350° C., the zeolite supported copper shows a NO<sub>x</sub> conversion under wet conditions of just under 20% whereas the ceria and zeolite shows an NO<sub>x</sub> conversion under wet conditions of just under 10%.

[0026] Referring to FIG. 2, it can be seen that the combination of a zeolite supported copper and ceria catalyst provides NO<sub>x</sub> conversions in the presence of water in excess of 40% at about 350° C. for both the silicon to aluminum ratios displayed in FIG. 2, that is a silicon to aluminum ratio of 67 and a silicon to aluminum ratio of 45. These conversions are outstanding. Only small amounts of NO<sub>2</sub> (<10 ppm) were observed, and no other nitrogen oxide species was present. Carbon dioxide was the only observable product from C<sub>3</sub>H<sub>6</sub> oxidation. The Cu-ZSM-5/CeO<sub>2</sub> catalyst had slightly lower maximum NO<sub>x</sub> activity than the Cu-ZSM-5. In all cases, the maximum NO<sub>x</sub> conversion approaches the temperature when the propene is nearly all consumed.

[0027] Under wet conditions, the Cu-ZSM-5 catalyst shows significant loss in NO<sub>x</sub> and hydrocarbon conversion activity. The CeO<sub>2</sub>/Cu-ZSM-5 catalyst shows improved NO<sub>x</sub> activity under wet conditions, possessing NO<sub>x</sub> conversion levels over 40%.

[0028] After reaction, the used catalysts were examined in the reactor prior to removal. It was noted that Cu-ZSM-5 catalyst showed significant discoloration throughout the bed, indicative of coking. However, with the other catalysts tested, it was observed that only a small fraction of the bed length was discolored, the rest of the bed remaining the same color as the original sample.

[0029] The ceria improves the Cu-ZSM-5 in two ways. First, it provides necessary water stability, most likely by drawing water away from the zeolite or active sites. Ceria also aids the NO<sub>x</sub> conversion reaction, based on improved activities with the CeO<sub>2</sub>/Cu-ZSM-5.

[0030] FIG. 3 shows similar data for a catalyst comprised of a zeolite supported copper with zirconia and a zeolite supported copper with molybdenum oxide. In these data it is clear that the zirconia containing catalyst is a superior performer at lower temperatures such as 400° C., whereas at 450° C. although the molybdenum containing catalyst is very good.

[0031] FIG. 4 shows a comparison of a cobalt and a combination of a zeolite supported cobalt with ceria. As can be seen from the data, without the ceria present there is little, if any, NO<sub>x</sub> under wet conditions whereas with the ceria present there is substantial conversion at 450° C.

[0032] FIG. 5 shows data for a variety of catalyst, the first being a zeolite supported copper with a combination of ceria and zirconia which shows excellent NO<sub>x</sub> conversions under wet conditions at about 400° C. and acceptable but less conversions at 350° C. Similarly, the copper cobalt supported zirconia with ceria shows excellent NO<sub>x</sub> conversions under wet conditions both at 400° and 350° C.

[0033] FIG. 6 illustrates comparisons of a mordenite supported copper and a mordenite supported copper with ceria under both wet and dry conditions. It is seen that the inventive catalyst, that is the copper supported mordenite with ceria has clearly superior activity at temperatures under 400° compared to the copper supported mordenite.

[0034] Finally in FIG. 7, shows data for a physical mixture of ceria and Cu-ZSM-5 and Cu-ZSM-5 on ceria. Note that these catalysts were tested at a space velocity of 10,000 Hr<sup>-1</sup> and 20% water when present. The physical mixture of Cu-ZSM-5 and CeO<sub>2</sub> showed no loss in activity, but only a

slight shift in temperature where the maximum activity occurred. In the case of Cu-ZSM-5/CeO<sub>2</sub>, there is still some loss of NO conversion, but not as great as the Cu-ZSM-5 alone, while hydrocarbon conversion remained high.

[0035] The date reported herein were for lean-burn combustion gases, that is combustion gases in which air or oxygen was present in greater than stoichiometric quantities. Moreover, all the data reported herein had between about 10 and 20% water present in the combustion gases.

[0036] While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A two phase catalyst comprising a molecular sieve having a pore size not less than about 4 Å supported transition metal and a stabilizing oxide.

2. The two phase catalyst of claim 1, wherein the molecular sieve is a zeolite of one or more of zeolite Y, zeolite beta, mordenite, ferrierite, ZSM-5, and ZSM-12.

3. The two phase catalyst of claim 2, wherein the transition metal is one or more of Cu, Co, Fe and Mo and the stabilizing oxide is one or more of the oxides of Ce, Zr, Mo, V and Nb.

4. The two phase catalyst of claim 1, wherein the two phases are a physical mixture.

5. The two phase catalyst of claim 1, wherein the zeolite is impregnated with the stabilizing oxide.

6. A two phase catalyst comprising a zeolite supported transition metal and a stabilizing oxide.

7. The two phase catalyst of claim 6, wherein the zeolite has a pore size not less than about 4 Å.

8. The two phase catalyst of claim 6, wherein the zeolite has a pore size in the range of from about 4 Å to about 8 Å.

9. The two phase catalyst of claim 6, wherein the zeolite is one or more of zeolite beta, mordenite, ferrierite, ZSM-5, ZSM-12, and zeolite Y.

10. The two phase catalyst of claim 7, wherein the transition metal is one or more of Cu, Co, Fe and Mo.

11. The two phase catalyst of claim 7, wherein the stabilizing oxide is one or more of the rare earth oxides, zirconium oxide, molybdenum oxide, vanadium oxide and niobium oxide.

12. The two phase catalyst of claim 10, wherein the stabilizing oxide one or more of the oxides of Ce, Zr, Mo, V and Nb.

13. The two phase catalyst of claim 12, wherein the transition metal includes Cu and the stabilizing oxide includes CeO<sub>2</sub>.

14. The two phase catalyst of claim 13, wherein the zeolite has both Al and Si and the Si to Al ratio is between about 238 and about 17.

15. The two phase catalyst of claim 6, wherein the two phases are a physical mixture.

16. The two phase catalyst of claim 6, wherein the stabilizing oxide is impregnated on the zeolite.

17. A method of remediating the concentration of nitrogen oxides (NO<sub>x</sub>) in the exhaust from lean burn combustion in the presence of water comprising contacting the exhaust containing water and NO<sub>x</sub> with one or more of an alkane or alkene reductant or mixtures thereof at a temperature of not

greater than about 600° C. with a two part catalyst comprising a molecular sieve having a pore size not less than about 4 Å supported transition metal and a stabilizing oxide.

**18.** The method of claim 17, wherein the molecular sieve is a zeolite.

**19.** The catalyst of claim 18, wherein the zeolite has a pore size in the range of from about 4 Å to about 8 Å.

**20.** The method of claim 18, wherein the zeolite is one or more of zeolite beta, mordenite, ferrierite, ZSM-5, ZSM-12, and zeolite Y.

**21.** The method of claim 17, wherein the transition metal is one or more of Cu, Co, Fe and Mo.

**22.** The method of claim 17, wherein the stabilizing oxide is one or more of the rare earth oxides, zirconium oxide, molybdenum oxide, vanadium oxide and niobium oxide.

**23.** The method of claim 18, wherein the stabilizing oxide is one or more of the oxides of Ce, Zr, Mo, V and Nb and the transition metal is one or more of Cu, Co, Fe and Mo.

**24.** The method of claim 23, wherein the transition metal includes Cu and the stabilizing oxide includes CeO<sub>2</sub>.

**25.** The method of claim 24, wherein the zeolite has both Al and Si and the Si to Al ratio is between about 238 and about 17.

**26.** The method of claim 17, wherein the reductant is a C<sub>1</sub> to C<sub>16</sub> hydrocarbon.

**27.** The method of claim 17, wherein nitrogen oxides are present in a concentration of the exhaust gas of not less than about 100 ppm.

**28.** The method of claim 17, wherein nitrogen oxides are present in a concentration of the exhaust gas in the range of from about 100 ppm to about 2000 ppm.

**29.** The method of claim 27, wherein the exhaust contacting the catalyst is at a temperature less than about 500° C.

**30.** The method of claim 27, wherein the exhaust contacting the catalyst is at a temperature less than about 350° C. and has water present in the exhaust at a concentration of not less than about 10% by volume.

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