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(54) Title: SMALL PORE MOLECULAR SIEVE SUPPORTED COPPER CATALYSTS DURABLE AGAINST LEAN/RICH AGING FOR THE REDUCTION OF NITROGEN OXIDES

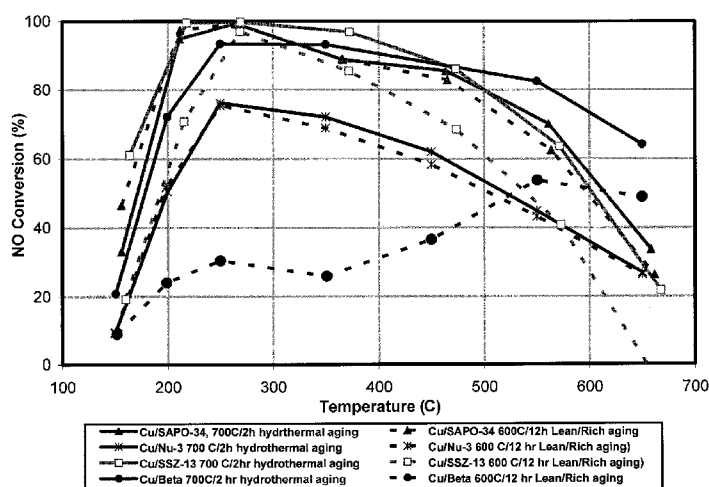


Figure 3

(57) Abstract: A method of using a catalyst comprises exposing a catalyst to at least one reactant in a chemical process. The catalyst comprises copper and a small pore molecular sieve having a maximum ring size of eight tetrahedral atoms. The chemical process undergoes at least one period of exposure to a reducing atmosphere. The catalyst has an initial activity and the catalyst has a final activity after the at least one period of exposure to the reducing atmosphere. The final activity is within 30% of the initial activity at a temperature between 200 and 500°C.

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SMALL PORE MOLECULAR SIEVE SUPPORTED COPPER CATALYSTS
DURABLE AGAINST LEAN/RICH AGING FOR THE REDUCTION OF NITROGEN OXIDES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application No. 61/170,358 and U.S. Provisional Application No. 61/312,832, both of which are herein incorporated by reference in their entireties for all purposes.

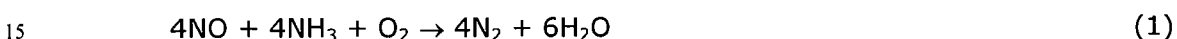
FIELD OF THE INVENTION

The present invention relates to small pore molecular sieve supported copper catalysts that are durable after being exposed to a reducing atmosphere, particularly after high temperature exposure.

5 BACKGROUND OF THE INVENTION

Selective catalytic reduction (SCR) of NO_x by nitrogenous compounds, such as ammonia or urea, has developed for numerous applications including for treating industrial stationary applications, thermal power plants, gas turbines, coal-fired power plants, plant and refinery heaters and boilers in the chemical processing industry, furnaces, coke ovens, municipal waste plants and incinerators, and a number of vehicular (mobile) applications, e.g., for treating diesel exhaust gas.

Several chemical reactions occur in an NH₃ SCR system, all of which represent desirable reactions that reduce NO_x to nitrogen. The dominant reaction is represented by reaction (1).



Competing, non-selective reactions with oxygen can produce secondary emissions or may unproductively consume ammonia. One such non-selective reaction is the complete oxidation of ammonia, shown in reaction (2).



20 Also, side reactions may lead to undesirable products such as N₂O, as represented by reaction (3).



Catalysts for SCR of NO_x with NH₃ may include, for example, aluminosilicate molecular sieves. One application is to control NO_x emissions from vehicular diesel engines, with the reductant obtainable from an ammonia precursor such as urea or by injecting ammonia *per se*. To promote the catalytic activity, transition metals may be incorporated into the aluminosilicate molecular sieves. The most commonly tested transition metal molecular sieves are Cu/ZSM-5, Cu/Beta, Fe/ZSM-5 and Fe/Beta because they have a relatively wide temperature activity window. In general, however, Cu-based molecular sieve catalysts show better low temperature NO_x reduction activity than Fe-based molecular sieve catalysts.

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In use, ZSM-5 and Beta molecular sieves have a number of drawbacks. They are susceptible to dealumination during high temperature hydrothermal ageing resulting in a loss of acidity, especially with Cu/Beta and Cu/ZSM-5 catalysts. Both beta- and ZSM-5-based catalysts are also affected by hydrocarbons which become adsorbed on the catalysts at relatively low temperatures and are oxidized as the temperature of the catalytic system is raised, generating a significant exotherm, which can thermally damage the catalyst. This problem is particularly acute in vehicular diesel applications where significant quantities of hydrocarbon can be adsorbed on the catalyst during cold-start; and Beta and ZSM-5 molecular sieves are also prone to coking by hydrocarbons.

In general, Cu-based molecular sieve catalysts are less thermally durable, and produce higher levels of N₂O than Fe-based molecular sieve catalysts. However, they have a desirable advantage in that they slip less ammonia in use compared with a corresponding Fe-molecular sieve catalyst.

WO 2008/132452 discloses a method of converting nitrogen oxides in a gas to nitrogen by contacting the nitrogen oxides with a nitrogenous reducing agent in the presence of a zeolite catalyst containing at least one transition metal, wherein the zeolite is a small pore zeolite containing a maximum ring size of eight tetrahedral atoms, wherein the at least one transition metal is selected from the group consisting of Cr, Mn, Fe, Co, Ce, Ni, Cu, Zn, Ga, Mo, Ru, Rh, Pd, Ag, In, Sn, Re, Ir and Pt.

WO 2008/106518 discloses a combination of a fiber matrix wall flow filter and a hydrophobic chabazite molecular sieve as a SCR catalyst on the fiber matrix wall flow filter. The filter purportedly achieves improved flexibility in system configuration and lower fuel costs for active regeneration. Such active regeneration would likely encompass exposure to lean atmospheric conditions. The reference, however, does not contemplate subjecting the filter to reducing conditions. The reference also fails to disclose or appreciate maintaining the durability of a catalyst after being exposed to such a reducing atmosphere.

SUMMARY OF THE INVENTION

According to one embodiment of the present invention, a method of using a catalyst comprises exposing a catalyst to at least one reactant in a chemical process. The catalyst comprises copper and a small pore molecular sieve having a maximum ring size of eight tetrahedral atoms. Preferably, the catalyst is a copper promoted small pore molecular sieve, i.e., a small pore molecular sieve loaded with copper. The chemical process undergoes at least one period of exposure to a reducing atmosphere. The catalyst has an initial activity and the catalyst has a final activity after the at least one period of exposure to the reducing atmosphere. The final activity is within 30% of the initial activity at a temperature between 200 and 500°C.

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According to another embodiment of the present invention, a method of using a catalyst comprises exposing a catalyst to at least one reactant comprising nitrogen oxides in a chemical process comprising exhaust gas treatment. The catalyst comprises copper and a small pore molecular sieve having a maximum ring size of eight tetrahedral atoms selected from the group of Framework Type Codes consisting of CHA, LEV, ERI and DDR. The chemical process undergoes at least one period of exposure to a reducing atmosphere. The catalyst has an initial activity, and the catalyst has a final activity after the at least one period of exposure to the reducing atmosphere. The final activity is within 10% of the initial activity at a temperature between 250 and 350 °C.

BRIEF DESCRIPTION OF THE DRAWINGS

In order that the invention may be more fully understood, reference is made to the following drawing by way of illustration only, in which:

Figure 1 is a graph illustrating NO_x conversion of medium pore and large pore molecular sieve supported copper catalysts after lean hydrothermal aging and lean/rich cycle aging;

Figure 2 is a graph illustrating NO_x conversion of Fe/molecular sieve catalysts after lean hydrothermal aging and lean/rich cycle aging;

Figure 3 is a graph illustrating NO_x conversion of small pore molecular sieve supported copper catalysts according to embodiments of the invention and a comparative Cu/Beta catalyst after lean hydrothermal aging and lean/rich cycle aging; and

Figure 4 is a graph illustrating NO_x conversion efficiency over a NAC and combined NAC+SCR systems with different SCR catalysts according to embodiments of the invention and comparative examples.

DETAILED DESCRIPTION OF THE INVENTION

A method of treating NO_x in an exhaust gas of a lean burn internal combustion engine is to store the NO_x from a lean gas in a basic material and then to release the NO_x from the basic material and reduce it periodically using a rich gas. The combination of a basic material (such as an alkali metal, alkaline earth metal or a rare earth metal), and a precious metal (such as platinum), and possibly also a reduction catalyst component (such as rhodium) is typically referred to as a NO_x adsorber catalyst (NAC), a lean NO_x trap (LNT), or a NO_x storage/reduction catalyst (NSRC). As used herein, NO_x storage/reduction catalyst, NO_x trap, and NO_x adsorber catalyst (or their acronyms) may be used interchangeably.

Under certain conditions, during the periodically rich regeneration events, NH₃ may be generated over a NO_x adsorber catalyst. The addition of a SCR catalyst downstream of the NO_x adsorber catalyst may 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

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reduce some or all of the NO_x that slips through the NAC catalyst during the normal lean operation conditions. As used herein, such combined systems may be shown as a combination of their respective acronyms, e.g., NAC+SCR or LNT+SCR.

The combined NAC+SCR system imposes additional requirements on the SCR catalyst component. Namely, besides having good activity and excellent thermal stability, the SCR catalyst has to be stable against lean/rich excursions. Such lean/rich excursions not only may occur during the regular NAC regeneration events, but also may happen during the NAC desulfation events. During the NAC desulfation events, the SCR catalyst may be exposed to temperatures much higher than it would be exposed to during the regular NO_x regeneration events. Therefore, a good SCR catalyst that is suitable for the NAC+SCR systems needs to be durable after being exposed to a reducing atmosphere at high temperature. Although the present invention is described herein with particular emphasis on the SCR embodiment, it is contemplated that the present invention may encompass any catalysts which lose activity when exposed to a reducing atmosphere.

Catalysts are often unstable when exposed to a reducing atmosphere, more particularly a high temperature reducing atmosphere. For example, copper catalysts are unstable during repeated lean/rich high temperature excursions, e.g., as is often encountered in vehicle exhaust gas or an exhaust gas treatment system. The reducing atmosphere occurs in the rich phase of a lean/rich excursion cycle. The reducing atmosphere conditions, however, can occur in a variety of environments including but not limited to environments typical for the regeneration or the desulfation of a NO_x adsorber catalyst, and for the active regeneration of a catalyzed soot filter, etc. Thus, as used herein, a reducing atmosphere is net reducing, for example, an exhaust gas having a lambda value of less than 1 (e.g., derived from an air/fuel ratio less than stoichiometric). Contrastingly, a non-reducing atmosphere is net oxidizing, e.g., having a lambda value greater than 1 (e.g., derived from an air/fuel ratio greater than stoichiometric).

Without wishing to be bound to a particular theory, it was believed prior to discovery of the present invention that molecular sieve supported copper catalysts would not maintain stability or activity when exposed to a reducing atmosphere (especially a reducing atmosphere encountered in a repeated lean/rich cycle excursions) because when exposed to the reducing atmosphere, the copper catalysts lost their activity. This loss of activity was suspected to be due to copper migration, sintering, and/or reduced copper dispersion. Surprisingly, we discovered in the present invention that small pore molecular sieve-supported copper catalysts maintained their catalytic activity even though the medium and large pore molecular sieve supported copper catalysts could not. It is believed that small pore molecular sieves provide a restriction on the copper from migrating out of the framework, sintering, losing copper dispersion, and beneficially resulting in an improved stability and activity of the catalyst. The medium and large pore

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molecular sieves, however, do not maintain their stability and activity when exposed to a reducing atmosphere possibly because of the effects of copper migration, sintering, and/or reduced copper dispersion.

According to one embodiment of the present invention, a method of using a catalyst comprises exposing a catalyst to at least one reactant in a chemical process. The catalyst comprises copper and a small pore molecular sieve having a maximum ring size of eight tetrahedral atoms. The chemical process undergoes at least one period of exposure to a reducing atmosphere. The catalyst has an initial activity and the catalyst has a final activity after the at least one period of exposure to the reducing atmosphere. The final activity is within 30% of the initial activity at a temperature between 150 and 650 °C, preferably between 200 and 500 °C.

A method of using a catalyst comprises exposing a catalyst to at least one reactant in a chemical process. As used herein, chemical process can include any suitable chemical process using a catalyst comprising a small pore molecular sieve comprising copper and encountering reducing conditions. Typical chemical processes include, but are not limited to, exhaust gas treatment such as selective catalytic reduction using nitrogenous reductants, lean NO_x catalyst, catalyzed soot filter, or a combination of any one of these with a NO_x adsorber catalyst or a three-way catalyst (TWC), e.g., NAC+(downstream)SCR or TWC+(downstream)SCR.

According to another aspect of the invention, provided is a system comprising NAC+(downstream)SCR or TWC+(downstream)SCR, wherein the SCR catalyst comprises a copper promoted small pore zeolite sieve as described here.

According to another aspect of the invention, provided is an SCR catalyzed soot filter wherein the SCR catalyst comprises a copper promoted small pore zeolite sieve as described here.

A method of using a catalyst comprises exposing a catalyst to at least one reactant. The reactant may include any reactants typically encountered in the chemical processes above. Reactants may include a selective catalytic reductant, such as ammonia. Selective catalytic reduction may include (1) using ammonia or a nitrogenous reductant or (2) a hydrocarbon reductant (the latter also known as lean NO_x catalysis). Other reactants may include nitrogen oxides and oxygen.

The catalyst comprises a transition metal, preferably copper, and a small pore molecular sieve having a maximum ring size of eight tetrahedral atoms. As is used herein "molecular sieve" is understood to mean a metastable material containing tiny pores of a precise and uniform size that may be used as an adsorbent for gases or liquids. The molecules which are small enough to pass through the pores are adsorbed while the larger molecules are not. The molecular sieve framework may be defined as is generally

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acceptable by the International Zeolite Association framework type codes (at <http://www.iza-online.org/>). These molecular sieves are described in more detail below.

Molecular sieves are typically defined by the member rings as follows: large pore rings are 12-member rings or larger; medium pore rings are 10-member rings; and small pore rings are 8-member rings or smaller. The catalyst in the present invention is a small pore ring having a maximum ring size of eight tetrahedral atoms.

Most catalysts are supported on medium pore (10-ring, such as ZSM-5) or large pore (12-ring, such as Beta) molecular sieves. A molecular sieve supported copper SCR catalyst, for example, may exhibit wide temperature windows under NO only conditions. These catalysts, however, are not stable against repeated lean/rich high temperature aging as is demonstrated in Figure 1. In Figure 1, a Cu/Beta catalyst (large pore) and a Cu/ZSM-5 catalyst (medium pore) are shown under hydrothermal aging conditions and lean/rich aging conditions. As is evidenced by the dotted lines representing the lean/rich aging conditions, these types of catalysts are not suitable when exposed to repeated reducing conditions. In particular, these catalysts are not suitable for NAC+SCR applications.

Molecular sieve supported iron SCR catalysts, although not as active as molecular sieve supported copper catalysts at low temperatures (e.g. $<350^{\circ}\text{C}$), are stable against repeated lean/rich high temperature aging as shown in Figure 2. In Figure 2, Fe/Ferrierite, Fe/ZSM-5, and Fe/Beta are shown after hydrothermal aging and lean/rich aging conditions. Accordingly, molecular sieve supported iron catalysts have been the technology of choice due to their excellent stability against cycled lean/rich aging, e.g., as is encountered in NAC+SCR applications.

Small pore molecular sieve supported Cu catalysts have been demonstrated to exhibit improved NH_3 -SCR activity and excellent thermal stability. According to one aspect of the invention, it was found that this type of catalyst also tolerates repeated lean/rich high temperature aging. Figure 3 compares a series of small pore molecular sieve supported Cu catalysts (Cu/SAPO-34, Cu/Nu-3, and Cu/SSZ-13, respectively) against a comparative large pore catalyst (Cu/Beta) after $700^{\circ}\text{C}/2$ hours hydrothermal aging and $600^{\circ}\text{C}/12$ hours cycled lean/rich aging, respectively. As is evident in Figure 3, the catalysts with small pore molecular sieve are very stable against lean/rich aging. In particular, the Cu/SAPO-34 catalyst exhibited exceptionally good low temperature activity and showed no activity degradation after cycled lean/rich aging, i.e., repeated exposure to a reducing atmosphere.

The catalysts in embodiments of the present invention show a much wider temperature window of high NO_x conversion. The temperature range of improved conversion efficiency may range from about 150 to 650°C , more particularly from 200 to 500°C , more particularly from 200 to 450°C , or most significantly from about 200 to

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400°C. In these temperature ranges, conversion efficiencies after exposure to a reducing atmosphere, and even after exposure to a reducing atmosphere and to high temperatures (e.g., up to 850 °C), may range from greater than 55% to 100%, more preferably greater than 90% efficiency, and even more preferably greater than 95% efficiency. In particular, combined NAC+SCR systems show a much wider temperature window of high NO_x conversion compared to either NAC catalysts alone or NAC+SCR systems using a Fe/molecular sieve SCR catalyst. See Figure 4. For example at about 250°C and about 300°C, the NO_x conversion efficiencies for systems subjected to lean/rich aging are as follows:

System (undergone lean/rich aging)	NO _x Conversion % at 250°C	NO _x Conversion % at 300°C
NAC alone	73	92
NAC + Fe/Beta SCR catalyst	87	90
NAC + Cu/SSZ-13 SCR catalyst	93	97
NAC + Cu/SAPO-34 SCR catalyst	97	96

As is evident from these results, the use of the NAC + Cu/small pore molecular sieve catalyst shows dramatic improvement in conversion efficiencies. These improvements are to the final NO_x emissions. Thus, an improvement from about 87% NO_x conversion (about 13% NO_x remaining) to about 97% NO_x conversion (about 3% NO_x remaining) is about a 433% improvement in efficiency, based on the percent NO_x remaining.

The catalyst has an initial activity and the catalyst has a final activity after the at least one period of exposure to the reducing atmosphere. In certain embodiments, catalyst activity is NO_x conversion efficiency. Accordingly, the initial activity is NO_x conversion efficiency of a catalyst that has not been exposed to a reducing atmosphere and the final activity is NO_x conversion efficiency of the catalyst after exposure to a reducing atmosphere. The initial activity may include a baseline aging under hydrothermal conditions. Hydrothermal conditions may include aging at 700 °C for 2 hours with 5% H₂O in air.

The chemical process undergoes at least one period of exposure to a reducing atmosphere. The reducing atmosphere may include any suitable reducing atmosphere such as during rich conditions in a lean/rich aging cycle. For example, a localized reducing atmosphere may also occur during catalyzed soot filter regeneration. The at least one period of exposure may include repeated exposures to reducing conditions or a prolonged exposure to reducing conditions. For example, a repeated exposure may include a cycled lean/rich aging at 600 °C for 12 hours. A lean cycle may last from 15 seconds to several tens of minutes, and a rich cycle may last from less than 1 second to several minutes. In

a NAC-SCR system or TWC-SCR system, the rich cycle may range, for example, from 1 to 60 continuous seconds, from 1 to 15 continuous seconds, or from 5 to 15 continuous seconds. In a coated soot filter application (e.g., a SCR/DPF (diesel particulate filter), the rich cycle may range, for example, from 30 seconds to 60 minutes of continuous exposure, from 5 minutes to 30 minutes of continuous exposure, or from 10 minutes to 30 minutes of continuous exposure. For example, the lean portion of the cycle may consist of exposure to 200 ppm NO, 10% O₂, 5% H₂O, 5% CO₂ in N₂, and the rich portion of the cycle may consist of exposure to 200 ppm NO, 5000 ppm C₃H₆, 1.3% H₂, 4% CO, 1% O₂, 5% H₂O, 5% CO₂ in N₂. The reducing atmosphere may be a high temperature reducing atmosphere. A high temperature reducing atmosphere may occur at a temperature from about 150°C to 850°C or more particularly from about 450°C to 850°C.

The final activity is within about 30%, more preferably within about 10%, more preferably within about 5%, even more preferably within about 3% of the initial activity at a catalytic operating temperature. Preferably, the catalytic operating temperature is between about 150 and about 650 °C and more preferably between about 200 and about 500 °C. While the activity of the catalyst is preferably measured within a temperature range of 200 and 500 °C, portions of the chemical process can operate at any temperature, for example, a wider temperature range including higher temperatures. For example, catalyst activity will still be maintained in the temperature range of 200 and 500 °C even after the catalyst has been exposed to higher temperatures, e.g. up to 850 °C. As used herein, when the final activity is given as a percentage of the initial activity, it is given as an average of percentages over the temperature range provided; in other words, if a final activity is said to be within 30% of the initial activity at a temperature between 200 and 500 °C, it need not be less than 30% at every temperatures tested in that range, but would merely average less than 30% over the temperatures tested. Moreover, while activity is identified as NO_x conversion in the examples of this application, the activity could be some other measure of catalyst activity depending on the chemical process, as is known in the art. The data showing catalyst activity and the percentage of initial activity to final activity is evidenced in the following tables (See also Figure 3). A negative number means that the activity after exposure to the reducing conditions actually improved relative to the initial activity (and therefore would certainly be "within" a certain positive percentage of the initial activity):

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For the embodiment using Cu/Nu-3 the following data was obtained:

TEMP	HT Aging	TEMP	LR Aging	%
150	9	150	9	-2%
200	50	198	52	-2%
250	76	250	75	1%
350	72	350	69	4%
450	62	450	58	6%
550	45	550	43	3%
650	27	650	26	2%

Thus, the lean/rich aging % NO_x reduction was within about 6% of the hydrothermal aging % NO_x reduction. Accordingly, the catalyst remained stable and had good activity following repeated exposure to reducing conditions throughout the temperature ranging from about 150 to about 650°C.

For the embodiment using Cu/SSZ-13 the following data was obtained:

TEMP	HT Aging	TEMP	LR Aging	%
164	61	160	19	68%
218	100	216	71	29%
269	100	269	97	3%
373	97	372	86	12%
473	86	474	68	20%
572	64	573	41	36%
668	22	669	-7	134%

Thus, the lean/rich aging % NO_x reduction was within about 30% of the hydrothermal aging % NO_x reduction throughout the temperature ranging from about 200 to about 500°C.

For the embodiment using Cu/SAPO34 the following data was obtained:

TEMP	HT Aging	TEMP	LR Aging	%
156	33	156	47	-41%
211	95	212	97	-3%
264	99	265	99	0.04%
366	89	366	89	-0.01%
464	86	465	83	3%
561	70	564	62	11%
658	34	662	26	22%

Thus, the lean/rich aging % NO_x reduction was within about 3% of the hydrothermal aging % NO_x reduction throughout the temperature ranging from about 200 to about 500°C, and within about 10% at temperatures ranging from about 200 to 560°C.

As a comparative example a Cu/Beta, large pore molecular sieve catalyst, was compared:

TEMP	HT Aging	TEMP	LR Aging	%
150	21	152	9	57%
200	72	199	24	67%
250	93	250	30	67%
350	93	351	26	72%
450	82	450	37	56%
550	82	550	54	35%
650	64	650	49	24%

The Cu/Beta comparative example showed poor activity following lean/rich cycled aging. Thus, exposure to a reducing atmosphere for the copper molecular sieve catalysts causes poor stability and activity as was contemplated prior to discovery of the present invention.

According to one embodiment of the present invention, a method of using a catalyst comprises exposing a catalyst to at least one reactant comprising nitrogen oxides in a chemical process comprising exhaust gas treatment. The catalyst comprises copper and a small pore molecular sieve having a maximum ring size of eight tetrahedral atoms selected from the group of Framework Type Codes consisting of CHA, LEV, ERI and DDR. The chemical process undergoes at least one period of exposure to a reducing atmosphere. The catalyst has an initial activity, and the catalyst has a final activity after the at least one period of exposure to the reducing atmosphere. The final activity is within 10% of the initial activity at a temperature between 250 and 350°C. In a preferred embodiment, the catalyst has a final activity that is within 3% of the initial activity at a temperature between 250 and 350°C.

In an embodiment of the invention, the catalysts have been combined with a NAC (NO_x adsorber catalyst) and tested as NAC+SCR systems. Figure 4 compares the NO_x reduction efficiency over a NAC alone and NAC+SCR systems with different SCR small pore molecular sieve catalysts (Cu/SAPO-34, and Cu/SSZ-13), and a comparative example of a Fe/beta catalyst. Combining an Fe/molecular sieve SCR with a NAC catalyst has been shown to improve the system NO_x conversion compared to NAC alone. Remarkably, however, the other two systems with a small pore molecular sieve comprising copper, i.e., Cu/SAPO-34 or Cu/SSZ-13, also exhibited further improved NO_x removal efficiency. This is especially evident at low temperatures (200-350°C). These results clearly suggest that small pore molecular sieve supported Cu catalysts offers new potential to further improve the performance of NAC+SCR systems.

In addition to NAC+SCR applications, the small pore molecular sieve supported Cu catalysts offer significant performance advantages for other applications that may be

exposed to a high temperature reducing atmosphere. For example, a small pore molecular sieve supported Cu catalyst may be used in a reducing atmosphere which occurs during active regeneration of a SCR/DPF (diesel particulate filter). Small pore molecular sieve supported Cu catalysts provide excellent thermal durability and exceptional stability against reducing conditions, e.g., rich aging that occurs in exhaust gas treatment systems.

It will be appreciated that by defining the molecular sieve by their Framework Type Codes we intend to include the "Type Material" and any and all isotypic framework materials. (The "Type Material" is the species first used to establish the framework type). Reference is made to Table 1, which lists a range of illustrative molecular sieve materials for use in the present invention. For the avoidance of doubt, unless otherwise made clear, reference herein to a molecular sieve by name, e.g. "chabazite", is to the molecular sieve material *per se* (in this example the naturally occurring type material chabazite) and not to any other material designated by the Framework Type Code to which the individual molecular sieve may belong, e.g. some other isotypic framework material. Use of a FTC herein is intended to refer to the Type Material and all isotypic framework materials defined by that FTC.

The distinction between molecular sieve type materials, such as naturally occurring (i.e. mineral) chabazite, and isotypes within the same Framework Type Code is not merely arbitrary, but reflects differences in the properties between the materials, which may in turn lead to differences in activity in the method of the present invention. It will be appreciated, e.g. from Table 1 hereinbelow, that by "MeAPSO" and "MeAIPO" we intend zeotypes substituted with one or more metals. Suitable substituent metals include one or more of, without limitation, As, B, Be, Co, Fe, Ga, Ge, Li, Mg, Mn, Zn and Zr.

In a particular embodiment, the small pore molecular sieve catalysts for use in the present invention can be selected from the group consisting of aluminosilicate molecular sieves, metal-substituted aluminosilicate molecular sieves and aluminophosphate molecular sieves. Aluminophosphate molecular sieves with application in the present invention include aluminophosphate (AIPO) molecular sieves, metal substituted (MeAIPO) molecular sieves, silico-aluminophosphate (SAPO) molecular sieves and metal substituted silico-aluminophosphate (MeAPSO) molecular sieves.

In one embodiment, the small pore molecular sieve is selected from the group of Framework Type Codes 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.

In an embodiment, the small pore molecular sieve containing a maximum ring size of eight tetrahedral atoms is selected from the group of Framework Type Codes consisting of CHA, LEV, ERI, and DDR. In a preferred embodiment, the small pore molecular sieve comprises a CHA Framework Type Code selected from SAPO-34 or SSZ-13. In another

embodiment, the small pore molecular sieve comprises a LEV Framework Type Code Nu-3. Additionally, the small pore molecular sieve may comprise an AEI Framework Type Code SAPO-18, an ERI Framework Type Code ZSM-34, and/or a DDR Framework Type Code sigma-1. The small pore molecular sieve may also include disordered molecular sieves, such as an intergrown or mixed phase AEI/CHA, AEI/SAV, etc.

Molecular sieves with application in the present invention can include those that have been treated to improve hydrothermal stability. Illustrative methods of improving hydrothermal stability include:

(i) Dealumination by: steaming and acid extraction using an acid or complexing agent e.g. (EDTA - ethylenediaminetetracetic acid); treatment with acid and/or complexing agent; treatment with a gaseous stream of SiCl_4 (replaces Al in the molecular sieve framework with Si);

(ii) Cation exchange - use of multi-valent cations such as La; and

(iii) Use of phosphorous containing compounds (see e.g. U.S. Patent No. 5,958,818).

Illustrative examples of suitable small pore molecular sieves are set out in Table 1.

Table 1: Small Pore Molecular Sieve

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
ACO	*ACP-1	3D	3.5 x 2.8, 3.5 x 3.5	Ring sizes - 8, 4
AEI	*AIPO-18	3D	3.8 x 3.8	Ring sizes - 8, 6, 4
	[Co-Al-P-O]-AEI			
	SAPO-18			
	SIZ-8			
	SSZ-39			
AEN	*AIPO-EN3	2D	4.3 x 3.1, 2.7 x 5.0	Ring sizes - 8, 6, 4
	AIPO-53(A)			
	AIPO-53(B)			
	[Ga-P-O]-AEN			
	CFSAPO-1A			

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	CoIST-2			
	IST-2			
	JDF-2			
	MCS-1			
	MnAPO-14			
	Mu-10			
	UiO-12-500			
	UiO-12-as			
AFN	*AIPO-14	3D	1.9 x 4.6, 2.1 x 4.9, 3.3 x 4.0	Ring sizes – 8, 6, 4
	[(C ₃ N ₂ H ₁₂)]-[Mn-Al-P-O]-AFN			
	GaPO-14			
AFT	*AIPO-52	3D	3.8 x 3.2, 3.8 x 3.6	Ring sizes – 8, 6, 4
AFX	*SAPO-56	3D	3.4 x 3.6	Ring sizes – 8, 6, 4
	MAPSO-56, M=Co, Mn, Zr			
	SSZ-16			
ANA	*Analcime	3D	4.2 x 1.6	Ring sizes – 8, 6, 4
	AlPO ₄ -pollucite			
	AlPO-24			
	Ammonioleucite			
	[Al-Co-P-O]-ANA			
	[Al-Si-P-O]-ANA			
	Cs- -[Al-Ge-O]-ANA			
	Cs- -[Be-Si-O]-ANA			
	Cs ₁₆ [Cu ₈ Si ₄₀ O ₉₆]-ANA			

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	Cs-Fe [Si-O]-ANA			
	Cs-Na-(H ₂ O) [Ga-Si-O]-ANA			
	[Ga-Ge-O]-ANA			
	K- [B-Si-O]-ANA			
	K- [Be-B-P-O]-ANA			
	Li- [Li-Zn-Si-O]-ANA			
	Li-Na [Al-Si-O]-ANA			
	Na- [Be-B-P-O]-ANA			
	(NH ₄) - [Be-B-P-O]-ANA			
	(NH ₄) - [Zn-Ga-P-O]-ANA			
	[Zn-As-O]-ANA			
	Ca-D			
	Hsianghualite			
	Leucite			
	Na-B			
	Pollucite			
	Wairakite			
APC	*AIPO-C	2D	3.7 x 3.4, 4.7 x 2.0	Ring sizes - 8, 6, 4
	AIPO-H3			
	CoAPO-H3			
APD	*AIPO-D	2D	6.0 x 2.3, 5.8 x 1.3	Ring sizes - 8, 6, 4
	APO-CJ3			
ATT	*AIPO-12-TAMU	2D	4.6 x 4.2, 3.8 x 3.8	Ring sizes - 8, 6, 4
	AIPO-33			

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimension-ality	Pore size (Å)	Additional info
	RMA-3			
CDO	*CDS-1	2D	4.7 x 3.1, 4.2 x 2.5	Ring sizes – 8, 5
	MCM-65			
	UZM-25			
CHA	*Chabazite	3D	3.8 x 3.8	Ring sizes – 8, 6, 4
	AIPO-34			
	[Al-As-O]-CHA			
	[Al-Co-P-O]-CHA			
	Co [Be-P-O]-CHA			
	Co ₃ (C ₆ N ₄ H ₂₄) ₃ (H ₂ O) ₉ [Be ₁₈ P ₁₈ O ₇₂]-CHA			
	[Co-Al-P-O]-CHA			
	Li-Na [Al-Si-O]-CHA			
	[Mg-Al-P-O]-CHA			
	[Si-O]-CHA			
	[Zn-Al-P-O]-CHA			
	[Zn-As-O]-CHA			
	CoAPO-44			
	CoAPO-47			
	DAF-5			
	GaPO-34			
	K-Chabazite			
	Linde D			
	Linde R			
	LZ-218			
	MeAPO-47			
	MeAPSO-47			

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	(Ni(deta) ₂)-UT-6			
	Phi			
	SAPO-34			
	SAPO-47			
	SSZ-13			
	UiO-21			
	Willhendersonite			
	ZK-14			
	ZYT-6			
DDR	*Deca-dodecasil 3R	2D	4.4 x 3.6	Ring sizes – 8, 6, 5, 4
	[B-Si-O]-DDR			
	Sigma-1			
	ZSM-58			
DFT	*DAF-2	3D	4.1 x 4.1, 4.7 x 1.8	Ring sizes – 8, 6, 4
	ACP-3, [Co-Al-P-O]-DFT			
	[Fe-Zn-P-O]-DFT			
	[Zn-Co-P-O]-DFT			
	UCSB-3GaGe			
	UCSB-3ZnAs			
	UiO-20, [Mg-P-O]-DFT			
EAB	*TMA-E	2D	5.1 x 3.7	Ring sizes – 8, 6, 4
	Bellbergite			
EDI	*Edingtonite	3D	2.8 x 3.8, 3.1 x 2.0	Ring sizes – 8, 4
	(C ₃ H ₁₂ N ₂) _{2.5} [Zn ₅ P ₅ O ₂₀]-EDI			

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	[Co-Al-P-O]-EDI			
	[Co-Ga-P-O]-EDI			
	Li- [Al-Si-O]-EDI			
	Rb ₇ Na (H ₂ O) ₃ [Ga ₈ Si ₁₂ O ₄₀]-EDI			
	[Zn-As-O]-EDI			
	K-F			
	Linde F			
	Zeolite N			
EPI	*Epistilbite	2D	4.5 x 3.7, 3.6 x 3.6	Ring sizes - 8, 4
ERI	*Erionite	3D	3.6 x 5.1	Ring sizes - 8, 6, 4
	AIPO-17			
	Linde T			
	LZ-220			
	SAPO-17			
	ZSM-34			
GIS	*Gismondine	3D	4.5 x 3.1, 4.8 x 2.8	Ring sizes - 8, 4
	Amicite			
	[Al-Co-P-O]-GIS			
	[Al-Ge-O]-GIS			
	[Al-P-O]-GIS			
	[Be-P-O]-GIS			
	(C ₃ H ₁₂ N ₂) ₄ [Be ₈ P ₈ O ₃₂]-GIS			
	(C ₃ H ₁₂ N ₂) ₄ [Zn ₈ P ₈ O ₃₂]-GIS			
	[Co-Al-P-O]-GIS			
	[Co-Ga-P-O]-GIS			

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	[Co-P-O]-GIS			
	Cs ₄ [Zn ₄ B ₄ P ₈ O ₃₂]-GIS			
	[Ga-Si-O]-GIS			
	[Mg-Al-P-O]-GIS			
	(NH ₄) ₄ [Zn ₄ B ₄ P ₈ O ₃₂]-GIS			
	Rb ₄ [Zn ₄ B ₄ P ₈ O ₃₂]-GIS			
	[Zn-Al-As-O]-GIS			
	[Zn-Co-B-P-O]-GIS			
	[Zn-Ga-As-O]-GIS			
	[Zn-Ga-P-O]-GIS			
	Garronite			
	Gobbinsite			
	MAPO-43			
	MAPSO-43			
	Na-P1			
	Na-P2			
	SAPO-43			
	TMA-gismondine			
GOO	*Goosecreekite	3D	2.8 x 4.0, 2.7 x 4.1, 4.7 x 2.9	Ring sizes – 8, 6, 4
IHW	*ITQ-32	2D	3.5 x 4.3	Ring sizes – 8, 6, 5, 4
ITE	*ITQ-3	2D	4.3 x 3.8, 2.7 x 5.8	Ring sizes – 8, 6, 5, 4
	Mu-14			
	SSZ-36			
ITW	*ITQ-12	2D	5.4 x 2.4, 3.9 x 4.2	Ring sizes – 8, 6, 5, 4

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
LEV	*Levyne	2D	3.6 x 4.8	Ring sizes – 8, 6, 4
	AIPO-35			
	CoDAF-4			
	LZ-132			
	NU-3			
	RUB-1 [B-Si-O]-LEV			
	SAPO-35			
	ZK-20			
	ZnAPO-35			
KFI	ZK-5	3D	3.9 x 3.9	Ring sizes – 8, 6, 4
	18-crown-6 [Al-Si-O]-KFI			
	[Zn-Ga-As-O]-KFI			
	(Cs,K)-ZK-5			
	P			
	Q			
MER	*Merlinoite	3D	3.5 x 3.1, 3.6 x 2.7, 5.1 x 3.4, 3.3 x 3.3	Ring sizes – 8, 4
	[Al-Co-P-O]-MER			
	Ba- [Al-Si-O]-MER			
	Ba-Cl- [Al-Si-O]-MER			
	[Ga-Al-Si-O]-MER			
	K- [Al-Si-O]-MER			
	NH ₄ - [Be-P-O]-MER			
	K-M			
	Linde W			
	Zeolite W			

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
MON	*Montesommaite	2D	4.4 x 3.2, 3.6 x 3.6	Ring sizes – 8, 5, 4
	[Al-Ge-O]-MON			
NSI	*Nu-6(2)	2D	2.6 x 4.5, 2.4 x 4.8	Ring sizes – 8, 6, 5
	EU-20			
OWE	*UIO-28	2D	4.0 x 3.5, 4.8 x 3.2	Ring sizes – 8, 6, 4
	ACP-2			
PAU	*Paulingite	3D	3.6 x 3.6	Ring sizes – 8, 6, 4
	[Ga-Si-O]-PAU			
	ECR-18			
PHI	*Phillipsite	3D	3.8 x 3.8, 3.0 x 4.3, 3.3 x 3.2	Ring sizes – 8, 4
	[Al-Co-P-O]-PHI			
	DAF-8			
	Harmotome			
	Wellsite			
	ZK-19			
RHO	*Rho	3D	3.6 x 3.6	Ring sizes – 8, 6, 4
	[Be-As-O]-RHO			
	[Be-P-O]-RHO			
	[Co-Al-P-O]-RHO			
	[H-][Al-Si-O]-RHO			
	[Mg-Al-P-O]-RHO			
	[Mn-Al-P-O]-RHO			
	[Na ₁₆ Cs ₈] [Al ₂₄ Ge ₂₄ O ₉₆]-RHO			
	[NH ₄]-[Al-Si-O]-RHO			

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	Rb- [Be-As-O]-RHO			
	Gallosilicate ECR-10			
	LZ-214			
	Pahasapaite			
RTH	*RUB-13	2D	4.1 x 3.8, 5.6 x 2.5	Ring sizes – 8, 6, 5, 4
	SSZ-36			
	SSZ-50			
SAT	*STA-2	3D	5.5 x 3.0	Ring sizes – 8, 6, 4
SAV	*Mg-STA-7	3D	3.8 x 3.8, 3.9 x 3.9	Ring sizes – 8, 6, 4
	Co-STA-7			
	Zn-STA-7			
SBN	*UCSB-9	3D	TBC	Ring sizes – 8, 4, 3
	SU-46			
SIV	*SIZ-7	3D	3.5 x 3.9, 3.7 x 3.8, 3.8 x 3.9	Ring sizes – 8, 4
THO	*Thomsonite	3D	2.3 x 3.9, 4.0 x 2.2, 3.0 x 2.2	Ring sizes – 8, 4
	[Al-Co-P-O]-THO			
	[Ga-Co-P-O]-THO			
	Rb ₂₀ [Ga ₂₀ Ge ₂₀ O ₈₀]-THO			
	[Zn-Al-As-O]-THO			
	[Zn-P-O]-THO			
	[Ga-Si-O]-THO)			
	[Zn-Co-P-O]-THO			
TSC	*Tschörtnerite	3D	4.2 x 4.2, 5.6 x 3.1	Ring sizes – 8, 6, 4

Molecular Sieve Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
UEI	*Mu-18	2D	3.5 x 4.6, 3.6 x 2.5	Ring sizes – 8, 6, 4
UFI	*UZM-5	2D	3.6 x 4.4, 3.2 x 3.2 (cage)	Ring sizes – 8, 6, 4
VNI	*VPI-9	3D	3.5 x 3.6, 3.1 x 4.0	Ring sizes – 8, 5, 4, 3
YUG	*Yugawaralite	2D	2.8 x 3.6, 3.1 x 5.0	Ring sizes – 8, 5, 4
	Sr-Q			
ZON	*ZAPO-M1	2D	2.5 x 5.1, 3.7 x 4.4	Ring sizes – 8, 6, 4
	GaPO-DAB-2			
	UIO-7			

Small pore molecular sieves with particular application for exposure to reducing conditions are set out in Table 2.

Table 2: Preferred Small Pore Molecular Sieves.

Structure	Molecular Sieve
CHA	SAPO-34
	AIPO-34
	SSZ-13
LEV	Levynite
	Nu-3
	LZ-132
	SAPO-35
	ZK-20
ERI	Erionite
	ZSM-34
	Linde type T
DDR	Deca-dodecasil 3R
	Sigma-1

Structure	Molecular Sieve
KFI	ZK-5
	18-crown-6
	[Zn-Ga-As-O]-KFI
EAB	TMA-E
PAU	ECR-18
MER	Merlinoite
AEI	SSZ-39
GOO	Goosecreekite
YUG	Yugawaralite
GIS	P1
VNI	VPI-9
AEI	SAPO-18

Molecular sieves for use in the present application include natural and synthetic molecular sieves, preferably synthetic molecular sieves because the molecular sieves can have a more uniform: silica-to-alumina ratio (SAR), crystallite size, crystallite morphology, and the absence of impurities (e.g. alkaline earth metals). Small pore aluminosilicate molecular sieves may have a silica-to-alumina ratio (SAR) of from 2 to 300, optionally 4 to 200, and preferably 8 to 150. It will be appreciated that higher SAR ratios are preferred to improve thermal stability but this may negatively affect transition metal exchange.

The at least one reactant may contact the catalyst at a gas hourly space velocity of from 5,000 hr⁻¹ to 500,000 hr⁻¹, optionally from 10,000 hr⁻¹ to 200,000 hr⁻¹.

Small pore molecular sieves for use in the invention may have three-dimensional dimensionality, i.e. a pore structure which is interconnected in all three crystallographic dimensions, or two-dimensional dimensionality. In one embodiment, the small pore molecular sieves for use in the present invention consist of molecular sieves having three-dimensional dimensionality. In another embodiment, the small pore molecular sieves for use in the present invention consist of molecular sieves having two-dimensional dimensionality.

In certain embodiments, the small pore molecular sieve comprises, consists essentially of, or consists of a disordered framework selected from the group consisting of ABC-6, AEI/CHA, AEI/SAV, AEN/UEI, AFS/BPH, BEC/ISV, beta, fuajasilite, ITE/RTH, KFI/SAV, lovdarite, montesommaite, MTT/TON, pentasils, SBS/STF, SSF/STF, SSZ-33, and ZSM-48. 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 and/or an AEI Framework Type Code of

selected from AIPO-18, SAPO-18, SIZ-8, or SSZ-39. In one embodiment, the mixed phase composition is an AEI/CHA-mixed phase composition. The ratio of each framework type in the 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
5 embodiment, the ratio of AEI/CHA may range from about 5/95 to about 40/60. It is envisioned that a disordered molecular sieve, such as AEI/CHA, will be used as the support for one or more transition metals, such as Cr, Mn, Fe, Co, Ce, Ni, Cu, Zn, Ga, Mo, Ru, Rh, Pd, Ag, In, Sn, Re, Ir, Pt, and mixtures thereof, preferably Cr, Mn, Fe, Co, Ce, Ni, Cu, Rh, Pd, Pt, and mixtures thereof, more preferably Fe and/or Cu, and most preferably copper.

10 The total of the copper metal that can be included in the molecular sieve can be from 0.01 to 20 wt%, based on the total weight of the catalyst. In one embodiment, the total of the copper that can be included can be from 0.1 to 10 wt%. In a particular embodiment, the total of copper that can be included is from 0.5 to 5 wt%. The copper
15 may be included in the molecular sieve by any feasible method. For example, it can be added after the molecular sieve has been synthesized, e.g. by incipient wetness or exchange process; or can be added during molecular sieve synthesis.

A preferred two dimensional small pore molecular sieve for use in the present invention consists of Cu/LEV, such as Cu/Nu-3, whereas a preferred copper-containing
20 three dimensional small pore molecular sieve/aluminophosphate molecular sieve for use in the present invention consists of Cu/CHA, such as Cu/SAPO-34 or Cu/SSZ-13.

The molecular sieve catalysts for use in the present invention can be coated on a suitable substrate monolith or can be formed as extruded-type catalysts, but are preferably used in a catalyst coating. In one embodiment, the molecular sieve catalyst is
25 coated on a flow-through monolith substrate (i.e. a honeycomb monolithic catalyst support structure with many small, parallel channels running axially through the entire part) or filter monolith substrate such as a wall-flow filter etc. The molecular sieve catalyst for use in the present invention can be coated, e.g. as a washcoat component, on a suitable monolith substrate, such as a metal or ceramic flow through monolith substrate
30 or a filtering substrate, such as a wall-flow filter or sintered metal or partial filter (such as is disclosed in WO 01/80978 or EP 1057519, the latter document describing a substrate comprising convoluted flow paths that at least slows the passage of soot therethrough). Alternatively, the molecular sieves for use in the present invention can be synthesized directly onto the substrate. Alternatively, the molecular sieve catalysts according to the
35 invention can be formed into an extruded-type flow through catalyst.

Washcoat compositions containing the molecular sieves for use in the present invention for coating onto the monolith substrate for manufacturing extruded type substrate monoliths can comprise a binder selected from the group consisting of alumina,

silica, (non molecular sieve) silica-alumina, naturally occurring clays, TiO_2 , ZrO_2 , and SnO_2 .

In one embodiment, the at least one reactant, e.g., nitrogen oxides, are reduced with the reducing agent at a temperature of at least 100°C . In another embodiment, the
5 at least one reactant are reduced with the reducing agent at a temperature from about 150°C to 750°C . In a particular embodiment, the temperature range is from 175 to 550°C , or more particularly from 175 to 400°C .

For a reactant including nitrogen oxides, the reduction of nitrogen oxides may be carried out in the presence of oxygen or in the absence of oxygen. The source of
10 nitrogenous reductant can be ammonia *per se*, hydrazine or any suitable ammonia precursor (such as urea ($(\text{NH}_2)_2\text{CO}$)), ammonium carbonate, ammonium carbamate, ammonium hydrogen carbonate or ammonium formate.

The method may be performed on a gas derived from a combustion process, such as from an internal combustion engine (whether mobile or stationary), a gas turbine and
15 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, coffee roasting plants, etc.

In a particular embodiment, the method is used for treating exhaust gas from a
20 vehicular internal combustion engine with a lean/rich cycle, such as a diesel engine, a gasoline engine, or an engine powered by liquid petroleum gas or natural gas.

For a reactant including nitrogen oxides, the nitrogenous reductant may be metered into the flowing exhaust gas only when it is determined that the molecular sieves catalyst is capable of catalyzing NO_x reduction at or above a desired efficiency, such as at
25 above 100°C , above 150°C or above 175°C . The determination by the control means can be assisted by one or more suitable sensor inputs indicative of a condition of the engine selected from the group consisting of: exhaust gas temperature, catalyst bed temperature, accelerator position, mass flow of exhaust gas in the system, manifold vacuum, ignition timing, engine speed, lambda value of the exhaust gas, the quantity of fuel injected in the
30 engine, the position of the exhaust gas recirculation (EGR) valve and thereby the amount of EGR and boost pressure.

Metering may be controlled in response to the quantity of nitrogen oxides in the exhaust gas determined either directly (using a suitable NO_x sensor) or indirectly, such as using pre-correlated look-up tables or maps - stored in the control means - correlating any
35 one or more of the abovementioned inputs indicative of a condition of the engine with predicted NO_x content of the exhaust gas.

The entire contents of any and all patents and references cited herein are incorporated herein by reference.

EXAMPLES

Although the invention is illustrated and described herein with reference to specific embodiments, the invention is not intended to be limited to the details shown. Rather, various modifications may be made in the details within the scope and range of equivalents of the claims and without departing from the invention.

1. Steady State SCR Evaluation

Steady-state selective catalytic reduction (SCR) activity tests were conducted in a quartz reactor of 24 inches in length, and uniformly heated by two tube furnace units of 12 inches length. Experiments were performed at a gas hourly space velocity of 30,000 hr^{-1} utilizing catalyst dimensions of 1 inch diameter x 1 inch length. All gas lines directly connected to the reactor were maintained at 130 °C by heating tape to prevent gas species adsorption on the walls of the gas line. Water vapor was provided by a water bomb, which was constantly maintained at 70°C.

Prior to reaching the catalyst bed, the feed gas was heated and mixed upstream in the reactor via an inert thermal mass. The temperature of the gas stream was monitored at the catalyst inlet, center of the catalyst bed, and at the outlet by k-type thermocouples. Reacted feed gas was analyzed by a FTIR downstream from the catalyst bed at a sampling rate of 1.25 s^{-1} . The composition of the inlet feed gas could be determined by sampling from a bypass valve located upstream of the reactor.

Steady-state SCR experiments were initially performed on catalyst samples that had been hydrothermally (HT) aged at 700°C for 2 hours in the presence of air containing 4.5% H_2O . All steady state experiments were conducted using a feed gas of NO and NH_3 containing 350 ppm of NO, with an ammonia-to-NO (ANR) ratio of 1 (i.e., 350 ppm of NH_3). The remainder of the feed gas composition was as follows: 14% O_2 , 4.6% H_2O , 5% CO_2 , balance N_2 . The steady-state NO_x conversion was determined at catalyst bed temperatures of 150°C, 200°C, 250°C, 350°C, 450°C, 550°C, and 650°C.

Catalysts were then aged under lean-rich cycling conditions at 600°C for 12 h. The lean portion of the cycle consisted of exposure to 200 ppm NO, 10% O_2 , 5% H_2O , 5% CO_2 in N_2 for 5 seconds at a space velocity of 30,000 h^{-1} . The rich portion of the cycle consisted of exposure to 200 ppm NO, 5000 ppm C_3H_6 , 1.3% H_2 , 4% CO, 1% O_2 , 5% H_2O , 5% CO_2 in N_2 for 15 seconds. After the aging, steady-state SCR experiments were performed as described above.

In Figure 3, the NO_x conversion efficiency is shown for embodiments of the present invention and a comparative example. Cu/SAPO-34, Cu/Nu-3 and Cu/SSZ-13, small pore molecular sieve catalysts according to embodiments of the invention, are shown after having undergone the above described hydrothermal aging treatment and lean/rich aging treatment, respectively. A comparative example showing Cu/Beta, a large pore molecular sieve catalyst, is also shown after both hydrothermal aging and lean/rich aging. As is

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evident, the small pore molecular sieve catalysts demonstrated enhanced NO_x conversion efficiencies especially in the temperature window of 200 to 500 °C.

2. NAC+SCR Experiments

NO_x adsorber catalyst (NAC) and SCR cores were initially hydrothermally aged at 750°C for 16 hours in a 4.5% H₂O in air gas mixture. Samples were then mounted in the same reactor setup described above with the NAC catalyst mounted directly in front of the SCR catalyst. The catalysts were aged at 600°C for 12 hours under the lean-rich aging conditions described above (5 seconds lean/15 seconds rich).

The catalysts were then cooled to 450°C under lean-rich cycling (60 seconds lean/5 seconds rich, same gas compositions). At 450°C, 25 lean-rich cycles were completed (60 seconds lean/5 seconds rich) with the last five cycles used to determine an average cycle NO_x conversion for the catalyst. After the 25th cycle, the catalyst was held under the lean gas composition for 5 minutes. The catalyst was then cooled and evaluated at 400°C, 350°C, 300°C, 250°C, 200°C, and 175°C following the aforementioned cycle procedure.

In Figure 4, the NO_x conversion efficiency is shown for embodiments of the present invention and two comparative examples. NAC+Cu/SAPO-34 and NAC+ Cu/SSZ-13, small pore molecular sieve catalysts according to embodiments of the invention are shown after having undergone the above described lean/rich aging treatment. A comparative example showing NAC alone and NAC+Fe/Beta, a large pore molecular sieve catalyst, is also shown after lean/rich aging. As is evident, the small pore molecular sieve catalysts demonstrate enhanced NO_x conversion efficiencies comparable to and/or better than NAC alone or NAC+Fe/Beta, especially in the temperature window of 250 to 450 °C.

While preferred embodiments of the invention have been shown and described herein, it will be understood that such embodiments are provided by way of example only. Numerous variations, changes and substitutions will occur to those skilled in the art without departing from the spirit of the invention. Accordingly, it is intended that the appended claims cover all such variations as fall within the spirit and scope of the invention.

What is Claimed:

1. A method for using a catalyst comprising exposing a catalyst to at least one reactant in a chemical process, wherein the catalyst comprises copper and a small pore molecular sieve, the chemical process undergoes at least one period of exposure to a reducing atmosphere, the catalyst has an initial activity before exposure to the reducing atmosphere and a final activity after the at least one period of exposure to the reducing atmosphere, wherein the final activity is within 30% of the initial activity at a temperature between 150 and 650°C.

2. A method for using a catalyst comprising:
exposing a catalyst comprising copper and a small-pore molecular sieve to a reducing atmosphere, and
contacting the catalyst with at least one reactant in a non-reducing atmosphere, wherein said contacting occurs subsequent to said exposing,
wherein the catalyst has an initial activity before exposure to the reducing atmosphere and a final activity after the at least one period of exposure to the reducing atmosphere, wherein the final activity is within 30% of the initial activity at a temperature between 150 and 650°C.

3. A method according to claim 1, wherein the catalyst has a final activity that is within 5% of the initial activity at a temperature between 200 and 500°C.

4. A method according to claim 1, wherein the catalyst has a final activity that is within 3% of the initial activity at a temperature between 250 and 350°C.

5. A method according to claim 1, wherein the at least one reactant comprises nitrogen oxides and a selective catalytic reductant.

6. A method according to claim 5, wherein the selective catalytic reductant comprises ammonia.

7. A method according to claim 6, wherein the at least one reactant further comprises oxygen.

8. A method according to claim 1, wherein the small pore molecular sieve is selected from the group consisting of aluminosilicate molecular sieves, metal-substituted aluminosilicate molecular sieves, and aluminophosphate molecular sieves.

9. A method according to claim 1, wherein the small pore molecular sieves is selected from the group of Framework Type Codes 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.

10. A method according to claim 1, wherein the small pore molecular sieves containing a maximum ring size of eight tetrahedral atoms is selected from the group of Framework Type Codes consisting of CHA, LEV, ERI and DDR.

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11. A method according to claim 1, wherein the small pore molecular sieve comprises a CHA Framework Type Code SAPO-34.

12. A method according to claim 1, wherein the small pore molecular sieve is selected from the group consisting of a CHA Framework Type Code SSZ-13, a LEV Framework Type Code Nu-3, an AEI Framework Type Code SAPO-18, an ERI Framework Type Code ZSM-34, a DDR Framework Type Code sigma-1, and mixtures thereof.

13. A method according to claim 1, wherein the at least one period of exposure to a reducing atmosphere is repeated exposure to a high temperature reducing atmosphere.

14. A method according to claim 13, wherein the high temperature reducing atmosphere occurs at a temperature from about 150°C to 850°C.

15. A method according to claim 1, wherein the at least one period of exposure to a reducing atmosphere occurs during a lean/rich aging cycle in an exhaust gas treatment system.

16. A method according to claim 15, wherein the lean/rich aging cycle occurs repeatedly.

17. A method according to claim 1, wherein the chemical process is selective catalytic reduction of NO_x in an internal combustion engine exhaust gas.

18. A method according to claim 1, wherein the chemical process is catalyzed soot filter regeneration.

19. A method according to claim 1, wherein the chemical process is lean NO_x trap and selective catalytic reduction.

20. A method of using a catalyst comprising exposing a catalyst to at least one reactant comprising nitrogen oxides in a chemical process comprising exhaust gas treatment, wherein the catalyst comprises copper and a small pore molecular sieve framework having a maximum ring size of eight tetrahedral atoms selected from the group of Framework Type Codes consisting of CHA, LEV, ERI and DDR, the chemical process undergoes at least one period of exposure to a reducing atmosphere, the catalyst has an initial activity, and the catalyst has a final activity after the at least one period of exposure to the reducing atmosphere, wherein the final activity is within 10% of the initial activity at a temperature between 250 and 350°C.

21. A method according to claim 20, wherein the catalyst has a final activity that is within 3% of the initial activity at a temperature between 250 and 350°C.

22. A method according to claim 1, wherein the activity is NO_x conversion.

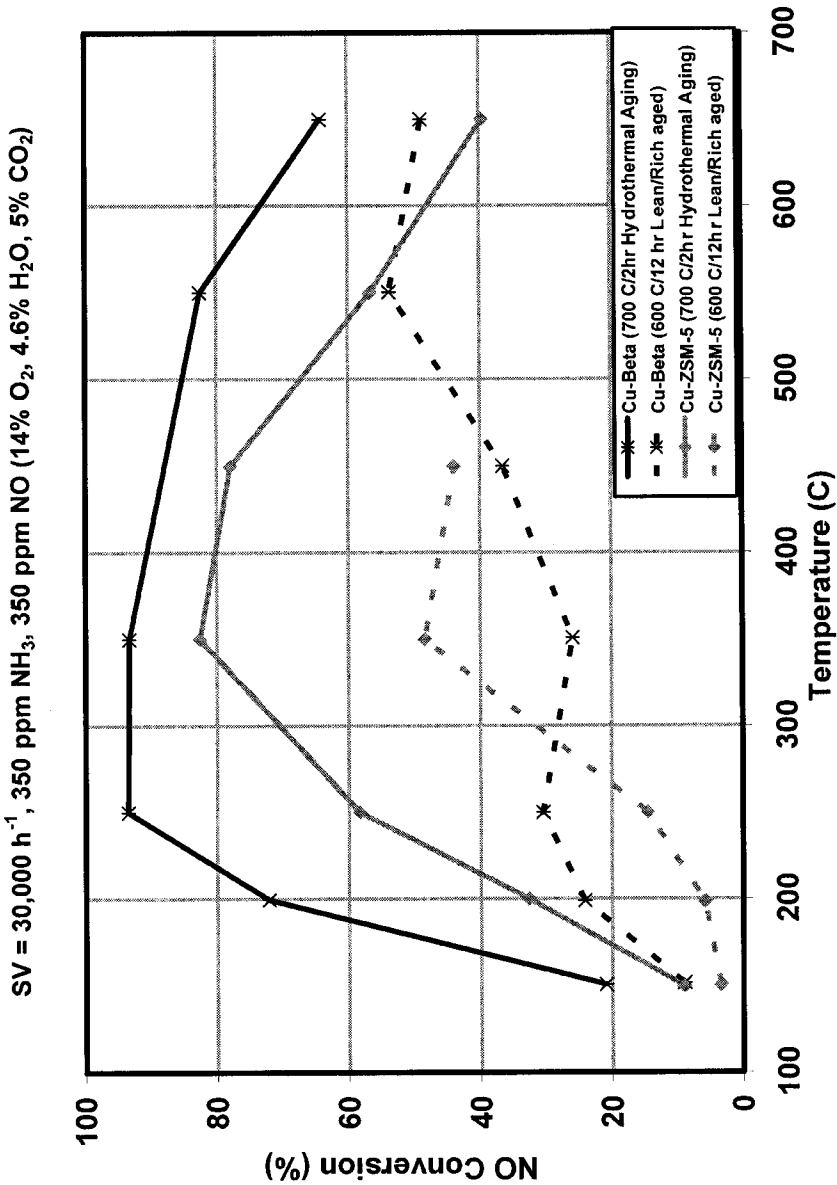


Figure 1

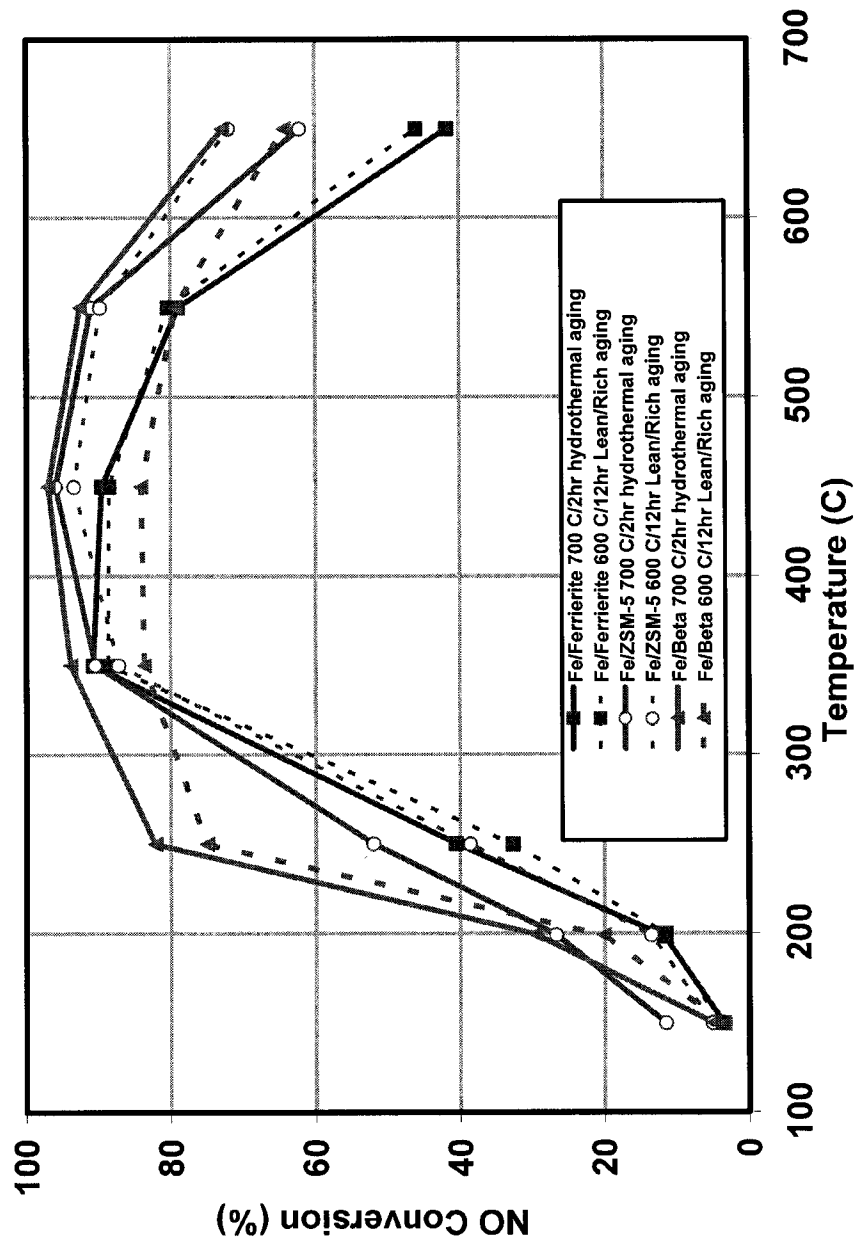


Figure 2

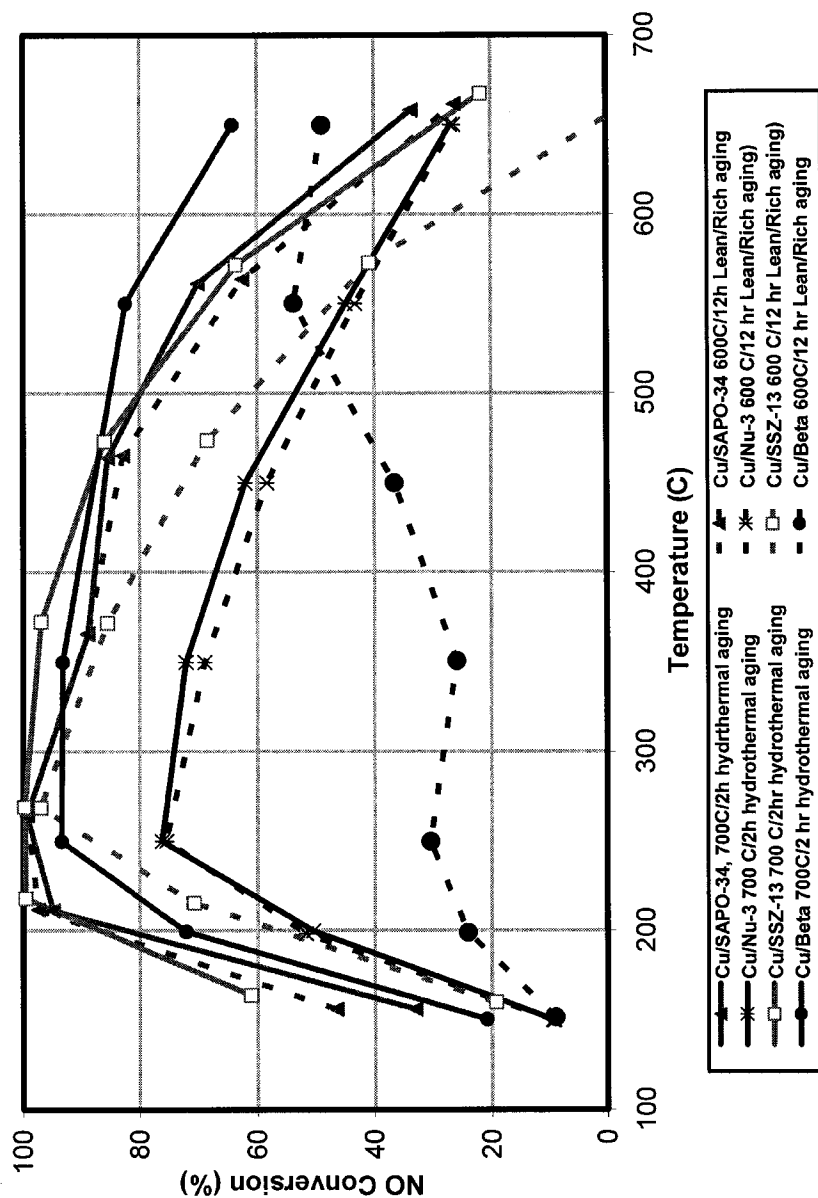


Figure 3

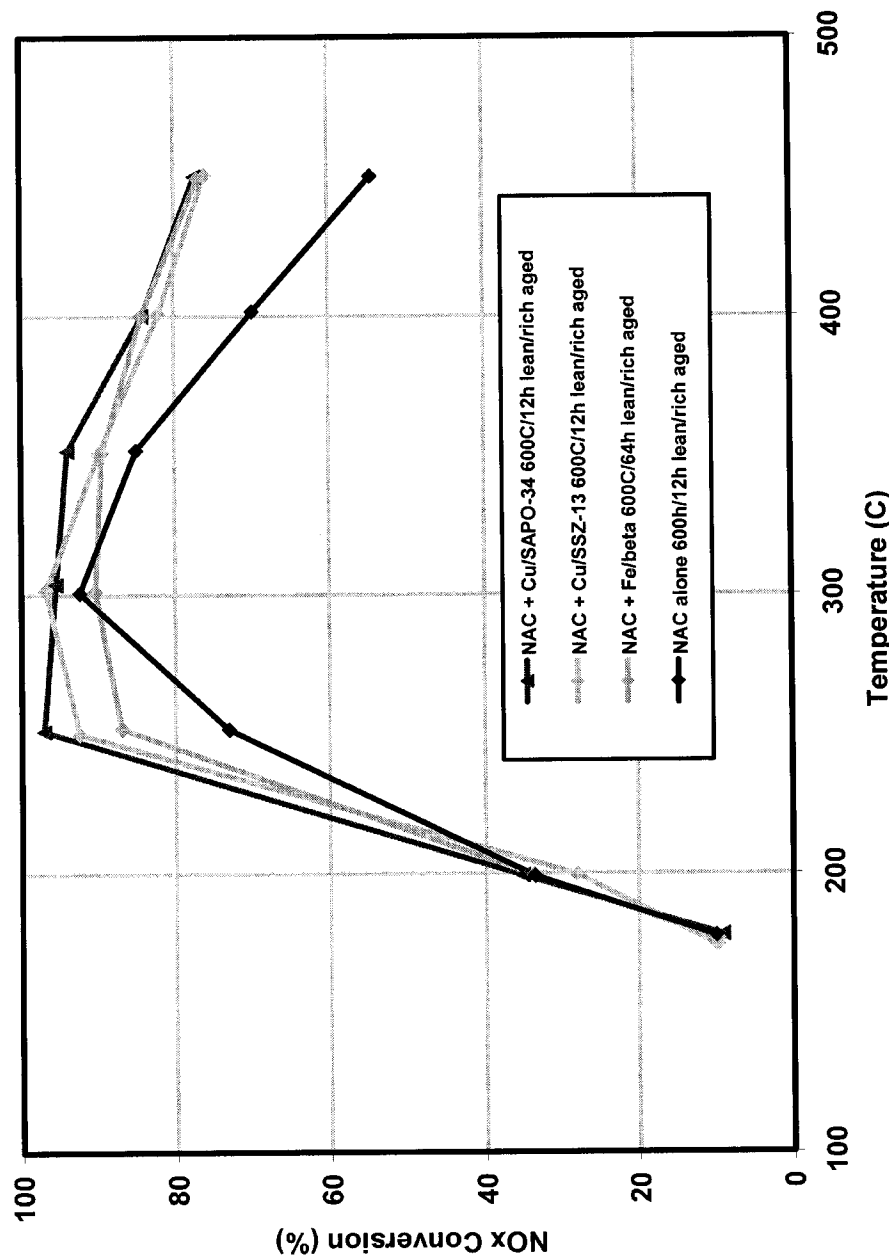


Figure 4

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/031617

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J29/072 B01D53/94
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ISHIHARA T ET AL: "Copper Ion-Exchanged SAPO-34 as a Thermostable Catalyst for Selective Reduction of NO with C3H6" JOURNAL OF CATALYSIS, ACADEMIC PRESS, DULUTH, MN, US LNKD-DOI:10.1006/JCAT.1997.1681, vol. 169, no. 1, 1 July 1997 (1997-07-01), pages 93-102, XP004465547 ISSN: 0021-9517	1-5, 7-17, 20-22
Y	* abstract page 93, right-hand column, last paragraph - page 94, left-hand column, paragraph 2nd page 98, right-hand column, last paragraph - page 101, left-hand column, paragraph 1st figures 11-13 ----- -/--	6, 18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 July 2010

Date of mailing of the international search report

23/07/2010

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/031617

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/202107 A1 (BOORSE SAMUEL [US] ET AL) 28 August 2008 (2008-08-28) claims 1,8-9,15,16 figure 3 paragraphs [0015], [0019], [0038] - [0040], [0050], [0064] - [0065] examples -----	6,18
X	WO 2008/132452 A2 (JOHNSON MATTHEY PLC [GB]; ANDERSEN PAUL JOSEPH [US]; BAILIE JILLIAN EL) 6 November 2008 (2008-11-06) cited in the application claims 1,9-16,21-23,28-31,35-37 figure 20; example 15 examples 2,6 -----	1-22

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-22(partially)

The present application contains 22 claims, of which three are independent in the same category. There is no clear distinction between the independent claims because of overlapping scope. Moreover, these claims relate to a method wherein the catalyst is defined (inter alia) by a desired property expressed as the following unusual parameter: "... an initial activity before exposure to the reducing atmosphere and a final activity after the at least one period of exposure to the reducing atmosphere, wherein the final activity is within 30% (10%) of the initial activity at a temperature between 150 and 650°C (250 and 350°C)." The use of this unusual parameter is considered to lead to a lack of clarity because the parameter cannot be clearly and reliably determined by indications in the description or by objective procedures which are usual in the art. The reaction is not defined in which the activity of the catalyst shall be determined, let alone any reaction conditions and which parameter actually shall be measured for determination of the activity. The wording of this feature "the final activity is within 30% of the initial activity" is unclear, especially if the description page 9 is taken into account where it seems that it is intended that the final activity shall not be less than 30% of the initial activity, while the expression used in the claims would be normally understood such that the final activity shall be lower than 30% of the initial activity. Beyond this, it is unclear what is meant by "the final activity is within 30% of the initial activity at a temperature between 150 and 650°C". From the wording it is completely open whether it is necessary that the final activity is within 30% of the initial activity over the whole range or whether it is sufficient that the final activity is within 30% of the initial activity for a certain temperature within this range. The description is not of much help since on page 8, lines 20-25 it is disclosed that it shall be understood as an average of percentages over the temperature range provided, while on page 9, it is disclosed as the maximum value within a certain temperature range. In addition, it is noted that it is not defined when the initial activity shall be determined. Many chemical processes have an induction period or the catalyst deactivates during the process, consequently it has a strong influence on the value obtained when the initial activity is measured. Similarly, for the final activity it is only disclosed that the measurement has to take place after the at least one period of exposure to the reducing temperature, but not how long after the reducing treatment this shall be. These unclarities make it impossible to compare the claims to the prior art. As a result, the application does not comply with the requirement of clarity under Article 6 PCT. In addition, the present claims relate to an extremely large number of possible methods. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the methods claimed. All examples in the present application refer to the selective catalytic reduction of nitrogen oxide with lean/rich cycles such that a reducing atmosphere occurs during the rich period and a non-reducing atmosphere is during the lean oxygen-rich period. Lastly, it is noted that the term "small pore molecular sieve" has no clear meaning in the art and should

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

be further defined by a maximum ring size of eight tetrahedral atoms and those framework type molecular sieves for which the effect was made credible. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search (PCT Guidelines 9.19 and 9.25). The search was based on the subject-matter that can be understood and seems to be supported in the description, namely - a method of using a catalyst in selective catalytic reduction of nitrogen oxides in a net non-reducing atmosphere, wherein the catalyst comprises copper and a small pore molecular sieve framework having a maximum ring size of eight tetrahedral atoms selected from the group of Framework Type Codes consisting of CHA, LEV, ERI and DDR, in the selective catalytic reduction the catalyst is exposed for at least one period to a net reducing atmosphere.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2010/031617

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-22(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/031617

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CA 2679590 A1	04-09-2008
		CN 101674876 A	17-03-2010
		CN 101668589 A	10-03-2010
		EP 2117681 A2	18-11-2009
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		US 2009285737 A1	19-11-2009
		WO 2008106518 A2	04-09-2008
		WO 2008106519 A1	04-09-2008
WO 2008132452 A2	06-11-2008	CA 2685009 A1	06-11-2008
		EP 2150328 A2	10-02-2010
		KR 20100017347 A	16-02-2010