(19) DANMARK

(10) DK/EP 2786796 T3

(12) Oversættelse af europæisk patentskrift

Patent- og Varemærkestyrelsen

(51) Int.Cl.: *B 01 D 53/94 (2006.01)* *B 01 J 23/72 (2006.01)* *B 01 J 23/745 (2006.01)* *B 01 J 29/56 (2006.01)* *B 01 J 29/70 (2006.01)* *B 01 J 29/85 (2006.01)*

(45) Oversættelsen bekendtgjort den: **2017-12-18**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2017-09-06**

(86) Europæisk ansøgning nr.: **14171510.2**

(86) Europæisk indleveringsdag: **2008-04-24**

(87) Den europæiske ansøgnings publiceringsdag: **2014-10-08**

(30) Prioritet: **2007-04-26 WO PCT/GB2007/050216**

(62) Stamansøgningsnr: **08762186.8**

(84) Designerede stater: **AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR**

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(54) Benævnelse: **KOBBER/AEI-ZEOLIT-SCR-KATALYSATOR**

(56) Fremdragne publikationer:
EP-A1- 2 944 377
WO-A1-2005/110582
DE-A1-102005 010 221
US-A- 5 958 370
US-A1- 2005 047 965
US-A1- 2007 000 243
US-B1- 6 717 025

DESCRIPTION

[0001] The present invention relates to an exhaust system for a vehicular lean burn internal combustion engine for converting nitrogen oxides in the exhaust gas to nitrogen by contacting the nitrogen oxides with a nitrogenous reducing agent in the presence of a transition metal-containing zeolite catalyst.

[0002] Selective catalytic reduction (SCR) of NO_x by nitrogenous compounds, such as ammonia or urea, was first developed for treating industrial stationary applications. SCR technology was first used in thermal power plants in Japan in the late 1970s, and has seen widespread application in Europe since the mid-1980s. In the USA, SCR systems were introduced for gas turbines in the 1990s and have been used more recently in coal-fired powerplants. In addition to coal-fired cogeneration plants and gas turbines, SCR applications include plant and refinery heaters and boilers in the chemical processing industry, furnaces, coke ovens, municipal waste plants and incinerators. More recently, NO_x reduction systems based on SCR technology are being developed for a number of vehicular (mobile) applications in Europe, Japan, and the USA, e.g. for treating diesel exhaust gas.

[0003] Several chemical reactions occur in an NH_3 SCR system, all of which represent desirable reactions that reduce NO_x to nitrogen. The dominant reaction is represented by reaction (1).

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

[0004] 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).

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (2)$$

Also, side reactions may lead to undesirable products such as N_2O, as represented by reaction (3).

$$4NH_3 + 5NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad (3)$$

[0005] Aluminosilicate zeolites are used as catalysts for SCR of NO_x with NH_3. 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 are incorporated into the aluminosilicate zeolites. The most commonly tested transition metal zeolites are Cu/ZSM-5, Cu/Beta, Fe/ZSM-5 and Fe/Beta because they have a relatively wide temperature activity window. In general, Cu-based zeolite catalysts show better low temperature NO_x reduction activity than Fe-based zeolite catalysts.

[0006] However, in use, ZSM-5 and Beta zeolites 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 oxidised 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 zeolites are also prone to coking by hydrocarbons.

[0007] In general, Cu-based zeolite catalysts are less thermally durable, and produce higher levels of N_2O than Fe-based zeolite catalysts. However, they have a desirable advantage in that they slip less ammonia in use compared with a corresponding Fe-zeolite catalyst.

[0008] It has been reported that aluminophosphate zeolites that contain transition metals demonstrate enhanced catalytic activity and superior thermal stability than aluminosilicate zeolite catalysts for SCR of NO_x with hydrocarbons (also known as lean NO_x catalysis or "DeNOx catalysts" (e.g. Ishihara et al., Journal of Catalysis, 169 (1997) 93)). In a similar vein, WO 2006/064805 discloses an electrical processing technology for treating diesel engine exhaust gas which utilizes corona discharge. A combination of a device for adding a NO_x reducer (hydrocarbon or fuel) and a Cu-SAPO-34 NO_x reducing catalyst can be disposed downstream of the electrical processing apparatus. However, to our knowledge, there has been no investigation of transition metal-containing aluminophosphate zeolites for SCR of NO_x with NH_3 (or urea) reported in any literature to date.

[0009] WO 00/72965 discloses iron (Fe) exchanged zeolites for the selective catalytic reduction of nitrogen monoxide by ammonia for controlling NO_x emissions from fossil-fuel power plants and engines. The Fe-exchanged, and optionally Fe-rare earth-exchanged, e.g. Fe-Ce-exchanged, zeolites suggested include: ZSM-5, mordenite, SAPO, clinoptilolite, chabazite, ZK-4 and ZK-5. No specific SAPO zeolites are identified and no experiment using SAPO zeolites is disclosed. Moreover, WO '965 teaches that the disclosure has application to zeolites with a range of pore sizes, i.e. large (mordenite), medium (ZSM-5, clinoptilolite) and small (chabazite, ZK-4, ZK-5) pore zeolites, with Fe-ZSM-5 preferred. There is no teaching or suggestion of any advantage in the use of small pore zeolites compared with medium and large pore zeolites. Moreover, ZK-4 zeolite is potentially hydrothermally unstable.

[0010] US patent no. 4,735,927 discloses an extruded-type NH_3-SCR catalyst with stability to sulfur poisoning comprising a high surface area titania in the form of anatase and a natural or

synthetic zeolite. The zeolite must be either in the acid form or thermally convertible to the acid form in the catalytic product. Examples of suitable zeolites include mordenite, natural clinoptilolite, erionite, heulandite, ferrierite, natural faujasite or its synthetic counterpart zeolite Y, chabazite and gmelinite. A preferred zeolite is natural clinoptilolite, which may be mixed with another acid stable zeolite such as chabazite. The catalyst may optionally include small amounts (at least 0.1% by elemental weight) of a promoter in the form of precursors of vanadium oxide, copper oxide, molybdenum oxide or combinations thereof (0.2 wt% Cu and up to 1.6 wt% V are exemplified). Extruded-type catalysts are generally less durable, have lower chemical strength, require more catalyst material to achieve the same activity and are more complicated to manufacture than catalyst coatings applied to inert monolith substrates.

[0011] US patent no. 5,417,949 also discloses an extruded-type NH_3-SCR catalyst comprising a zeolite having a constraint index of up to 12 and a titania binder. Intentionally, no transition metal promoter is present. ("Constraint Index" is a test to determine shape-selective catalytic behaviour in zeolites. It compares the reaction rates for the cracking of *n*-hexane and its isomer 3-methylpentane under competitive conditions (see V.J. Frillette et al., J Catal. 67 (1991) 218)).

[0012] US patent no. 5,589,147 discloses an ammonia SCR catalyst comprising a molecular sieve and a metal, which catalyst can be coated on a substrate monolith. The molecular sieve useful in the invention is not limited to any particular molecular sieve material and, in general, includes all metallosilicates, metallophosphates, silicoaluminophosphates and layered and pillared layered materials. The metal is typically selected from at least one of the metals of Groups of the Periodic Table IIIA, IB, IIB, VA, VIA, VIIA, VIIIA and combinations thereof. Examples of these metals include at least one of copper, zinc, vanadium, chromium, manganese, cobalt, iron, nickel, rhodium, palladium, platinum, molybdenum, tungsten, cerium and mixtures thereof.

[0013] The disclosure of US 5,589,147 is ambiguous about whether small pore zeolites (as defined herein) have any application in the process of the invention. For example, on the one hand, certain small pore zeolites are mentioned as possible zeolites for use in the invention, i.e. erionite and chabazite, while, among others, the molecular sieve SAPO-34 was "contemplated". On the other hand, a table is presented listing Constraint Index (CI) values for some typical zeolites "including some which are suitable as catalysts in the process of this invention". The vast majority of the CI values in the table are well below 10, of which erionite (38 at 316°C) and ZSM-34 (50 at 371°C) are notable exceptions. However, what is clear is that intermediate pore size zeolites, e.g. those having pore sizes of from about 5 to less than 7 Angstroms, are preferred in the process of the invention. In particular, the disclosure explains that intermediate pore size zeolites are preferred because they provide constrained access to and egress from the intracrystalline free space: "The intermediate pore size zeolites...have an effective pore size such as to freely sorb normal hexane...if the only pore windows in a crystal are formed by 8-membered rings of oxygen atoms, then access to molecules of larger cross-section than normal hexane is excluded and the zeolite is not an intermediate pore size material." Only extruded Fe-ZSM-5 is exemplified.

[0014] WO 2004/002611 discloses an NH_3-SCR catalyst comprising a ceria-doped aluminosilicate zeolite.

[0015] US 6,514,470 discloses a process for catalytically reducing NO_x in an exhaust gas stream containing nitrogen oxides and a reductant material. The catalyst comprises an aluminium-silicate material and a metal in an amount of up to about 0.1 weight percent based on the total weight of catalyst. All of the examples use ferrierite.

[0016] Long et al. Journal of Catalysis 207 (2002) 274-285 reports on studies of Fe^{3+}-exchanged zeolites for selective catalytic reduction of NO with ammonia. The zeolites investigated were mordenite, clinoptilolite, Beta, ferrierite and chabazite. It was found that in the conditions studied that the SCR activity decreases in the following order: Fe-mordenite > Fe-clinoptilolite > Fe-ferrierite > Fe-Beta > Fe-chabazite. The chabazite used for making the Fe-chabazite was a naturally occurring mineral.

[0017] US patent no. 4,961,917 discloses an NH_3-SCR catalyst comprising a zeolite having a silica-to-alumina ratio of at least about 10, and a pore structure which is interconnected in all three crystallographic dimensions by pores having an average kinetic pore diameter of at least about 7 Angstroms and a Cu or Fe promoter. The catalysts are said to have high activity, reduced NH_3 oxidation and reduced sulphur poisoning. Zeolite Beta and zeolite Y are two zeolites that meet the required definition.

[0018] US patent no. 3,895,094 discloses an NH_3-SCR process using zeolite catalysts of at least 6 Angstrom intercrystalline pore size. No mention is made of exchanging the zeolites with transition metals.

[0019] US patent no. 4,220,632 also discloses an NH_3-SCR process, this time using 3-10 Angstrom pore size zeolites of Na or H form.

[0020] WO 02/41991 discloses metal promoted zeolite Beta for NH_3-SCR, wherein the zeolite is pre-treated so as to provide it with improved hydrothermal stability.

[0021] US patent publication no. 2005/0047965 A1 discloses a catalyst sampling system, in particular a method and apparatus for obtaining a reproducible sample of solid particles. The reproducible sample is obtained by receiving solid particles into a collection system that includes a sheltered volume. Solid particles that settle outside of the sheltered volume are purged from the collection system. The remaining solid particles inside the sheltered volume correspond to the reproducible sample.

[0022] US patent no. 6717025 discloses a process for removing oxygenate impurities, e.g., dimethyl ether, from an olefinic product stream by converting the oxygenate impurity to a compound whose boiling point differs by at least about 5°C from the oxygenate impurity.

[0023] DE 102005010221 A1 discloses a method for preparing a catalytically active mineral having a framework silicate according to which the skeleton silicate is first treated with a metal salt solution and then dried, characterized in that the dried tectosilicate is treated in the hydrogen form with a metal salt based on copper in the course of a solid ion exchange.

[0024] WO 2005/110582 A1 discloses a method for the catalytic decomposition of N_2O in a gas containing N_2O in the presence of a catalyst, wherein the catalyst comprises a zeolite that has been loaded with a first metal selected from the group of noble metals consisting of ruthenium, rhodium, silver, rhenium, osmium, iridium, platinum and gold, and with a second metal selected from the group of transition metals consisting of chromium, manganese, iron, cobalt, nickel and copper, and wherein the loading of the zeolite with metals has been obtained by the first loading the zeolite with the noble metal and then with the transition metal.

[0025] US patent no. 5958370 discloses a crystalline zeolite designated SSZ-39 prepared using a cyclic or polycyclic quaternary ammonium cation templating agent. The document suggests that SSZ-39 containing a metal or metal ions can be used for catalyzing the reduction of nitrogen oxides in the exhaust gas from an internal combustion engine with simultaneous catalytic oxidation of carbon monoxide and hydrocarbons in the so-called three-way catalyst reaction.

[0026] EP 2944377 A1 discloses a hydrothermally stable microporous crystalline material comprising a molecular sieve or zeolite having an 8-ring pore opening structure, such as SAPO-34 or aluminosilicate zeolite, able to retain a specific percentage of its surface area and micro pore volume after treatment with heat and moisture, such as at least 80% of its surface area and micropore volume after exposure to temperatures of up to 900°C in the presence of up to 10 volume percent water vapor for a time ranging from 1 to 16 hours. Methods of using the disclosed crystalline material, such as in the SCR of NOx in exhaust gas are also disclosed, as are methods of making such materials.

[0027] There is a need in the art for SCR catalysts that have relatively good low temperature SCR activity, that have relatively high selectivity to N_2 - in particular low N_2O formation, that have relatively good thermal durability and are relatively resistant to hydrocarbon inhibition. We have now discovered a family of transition metal-containing zeolites that meet or contribute to this need.

[0028] According to one aspect, the invention provides an exhaust system for a vehicular lean burn internal combustion engine, which system comprising a conduit for carrying a flowing exhaust gas, a source of nitrogenous reductant, an extruded-type catalyst formed from a zeolite catalyst disposed in a flow path of the exhaust gas, means for metering nitrogenous reductant into a flowing exhaust gas upstream of the extruded-type catalyst and an oxidation catalyst comprising at least one platinum group metal for oxidising nitrogen monoxide to nitrogen dioxide located upstream of the means for metering nitrogenous reductant into a flowing exhaust gas, wherein the zeolite catalyst is a small pore zeolite containing a maximum

ring size of eight tetrahedral atoms and having the AEI Framework Type Code and wherein the total at least one transition metal present in the catalyst is from 0.5 to 5wt%, based on the total weight of the zeolite catalyst, wherein the at least one transition metal is copper.

[0029] By "zeolite catalyst containing at least one transition metal" herein we mean a zeolite structure to which has been added by ion exchange, impregnation or isomorphous substitution etc. one or more metals. "Transition metal-containing zeolite catalyst" and "zeolite catalyst containing at least one transition metal" and similar terms are used interchangeably herein.

[0030] It will be appreciated that by defining the zeolites 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 zeolite zeotype framework materials for use in the present invention. For the avoidance of doubt, unless otherwise made clear, reference herein to a zeolite by name, e.g. "chabazite", is to the zeolite 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 zeolite may belong, e.g. some other isotypic framework material. So for example, where the attached claims disclaim a zeolite catalyst, this disclaimer should be interpreted narrowly, so that "wherein the transition metal-containing small pore zeolite is not Cu/chabazite" is intended to exclude the type material and not any isotypic framework materials such as SAPO-34 or SSZ-13. Equally, use of a FTC herein is intended to refer to the Type Material and all isotypic framework materials defined by that FTC. For further information, we direct the reader to the website of the International Zeolite Association at www.iza-online.org.

[0031] The distinction between zeolite 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. For example, in addition to the comments made hereinbelow with reference to Long et al. Journal of Catalysis 207 (2002) 274-285, the naturally occurring chabazite has a lower silica-to-alumina ratio than alumino silicate isotypes such as SSZ-13, the naturally occurring chabazite has lower acidity than alumino silicate isotypes such as SSZ-13 and the activity of the material in the method of the present invention is relatively low (see the comparison of Cu/naturally occurring chabazite with Cu/SAPO-34 in Example 13).

[0032] The zeolite catalysts for use in the present invention are formed as extruded-type catalysts.

[0033] Whilst the prior art (such as the documents discussed in the background section hereinabove) does mention a few small pore zeolites containing at least one transition metal for converting nitrogen oxides in a gas to nitrogen with a nitrogenous reducing agent, there is no appreciation in the prior art that we can find of the particular advantages of using small pore zeolites containing at least one transition metal for this purpose. Thus, the prior art suggests

using large, medium and small pore zeolites containing at least one transition metal, without distinction.

[0034] It will be appreciated that chabazite is a small pore zeolite according to the definition adopted herein and that the Long *et al.* paper mentioned above reports that Fe/chabazite has the poorest activity of any of the catalysts tested. Without wishing to be bound by any theory, we believe that the poor performance of the Fe/chabazite in this study is due to two principal reasons. Firstly, natural chabazite can contain basic metal cations including potassium, sodium, strontium and calcium. To obtain an active material the basic metal cations need to be exchanged for e.g. iron cations because basic metals are a known poison of zeolite acid sites. In the reported study the natural mineral is first treated with NH_4Cl solution in an attempt to "flush out" the existing cations. However, we believe that one explanation for the poor reported activity is that the acidic sites in the chabazite of this study remain poisoned by basic metal cations.

[0035] Secondly, iron ions can form metal complexes (coordination compounds) with suitable ligands in the ionic exchange medium. In this regard we note that Long *et al.* use an aqueous $FeCl_2$ solution for ion exchange. Since the zeolite pores are relatively small, it is possible that a bulky co-ordination compound may not be able to gain access to the active sites located in the pores.

[0036] It will be appreciated, e.g. from Table 1 hereinbelow that by "MeAPSO" and "MeAlPO" 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.

[0037] In a particular embodiment, the small pore zeolites for use in the present invention can be selected from the group consisting of aluminosilicate zeolites, metal-substituted aluminosilicate zeolites and aluminophosphate zeolites.

[0038] Aluminophosphate zeolites with application in the present invention include aluminophosphate (AlPO) zeolites, metal substituted zeolites (MeAlPO) zeolites, silico-aluminophosphate (SAPO) zeolites and metal substituted silico-aluminophosphate (MeAPSO) zeolites.

[0039] It will be appreciated that the extruded-type substrate monoliths for use in the invention can comprise combinations of two or more transition metal-containing small pore zeolites.

[0040] In this invention, we have discovered that transition metal-containing small pore zeolites are advantageous catalysts for SCR of NO_x with NH_3. Compared to transition metal-containing medium, large or meso-pore zeolite catalysts, transition metal-containing small pore zeolite catalysts demonstrate significantly improved NO_x reduction activity, especially at low temperatures. They also exhibit high selectivity to N_2 (e.g. low N_2O formation) and good hydrothermal stability. Furthermore, small pore zeolites containing at least one transition metal

are more resistant to hydrocarbon inhibition than larger pore zeolites, e.g. a medium pore zeolite (a zeolite containing a maximum ring size of 10) such as ZSM-5 or a large pore zeolite (a zeolite having a maximum ring size of 12), such as Beta. Small pore aluminophosphate zeolites for use in the present invention include SAPO-18.

[0041] Zeolites with application in the present invention can include those that have been treated to improve hydrothermal stability. Illustrative methods of improving hydrothermal stability include:

1. (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 A1 in the zeolite framework with Si);
2. (ii) Cation exchange - use of multi-valent cations such as La; and
3. (iii) Use of phosphorous containing compounds (see e.g. US patent no. 5,958,818).

[0042] We believe that small pore zeolites may minimise the detrimental effect of hydrocarbons by means of a molecular sieving effect, whereby the small pore zeolite allows NO and NH_3 to diffuse to the active sites inside the pores but that the diffusion of hydrocarbon molecules is restricted. In this regard, the kinetic diameter of both NO (3.16Å) and NH_3 (2.6Å) is smaller than those of the typical hydrocarbons (C_3H_6 ~ 4.5Å, n-C_8H_{18} ~4.30Å and C_7H_8 ~ 6.0Å) present in, for example, diesel engine exhaust. Accordingly, in one embodiment the small pore zeolite catalysts for use in the present invention have a pore size in at least one dimension of less than 4.3 Å. Illustrative examples of suitable small pore zeolites are set out in Table 1.

Table 1: Details of small pore zeolites, some with application in the present invention

Zeolite 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	*AlPO-18	3D	3.8 x 3.8	Ring sizes - 8, 6, 4
	[Co-Al-P-O]-AEI			
	SAPO-18			
	SIZ-8			
	SSZ-39			
AEN	*AlPO-EN3	2D	4.3 x 3.1, 2.7 x 5.0	Ring sizes - 8, 6, 4
	AlPO-53(A)			

Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	AlPO-53(B)			
	[Ga-P-O]-AEN			
	CFSAPO-1A			
	CoIST-2			
	IST-2			
	JDF-2			
	MCS-1			
	MnAPO-14			
	Mu-10			
	UiO-12-500			
	UiO-12-as			
AFN	*AlPO-14	3D	1.9 x 4.6, 2.1 x 4.9, 3.3 x 4.0	Ring sizes - 8, 6, 4
	$\|(C_3N_2H_{12})$-$\|$[Mn-AlP-O]-AFN			
	GaPO-14			
AFT	*AlPO-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			
	$\|Cs_{16}\|[Cu_8Si_{40}O_{96}]$-ANA			

Zeolite 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_2O)|[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	*AlPO-C	2D	3.7 x 3.4, 4.7 x 2.0	Ring sizes - 8, 6, 4
	AlPO-H3			
	CoAPO-H3			
APD	*AlPO-D	2D	6.0 x 2.3, 5.8 x 1.3	Ring sizes - 8, 6, 4
	APO-CJ3			
ATT	*AlPO-12-TAMU	2D	4.6 x 4.2, 3.8 x 3.8	Ring sizes - 8, 6, 4
	AlPO-33			
	RMA-3			
CDO	*CDS-1	2D	4.7 x 3.1, 4.2 x 2.5	Ring sizes - 8, 5
	MCM-65			
	UZM-25			

Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
CHA	*Chabazite	3D	3.8 x 3.8	Ring sizes - 8, 6, 4
	AlPO-34			
	[Al-As-O]-CHA			
	[Al-Co-P-O]-CHA			
	|Co| [Be-P-O]-CHA			
	$\|Co_3(C_6N_4H_{24})_3(H_2O)_9\|$ $[Be_{18}P_{18}O_{72}]$-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			
	$(Ni(deta)_2)$-UT-6			
	Phi			
	SAPO-34			
	SAPO-47			
	SSZ-13			
	UiO-21			
	Willhendersonite			
	ZK-14			

Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	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
	$\lvert(C_3H_{12}N_2)_{2.5}\rvert$ $[Zn_5P_5O_{20}]$-EDI			
	[Co-Al-P-O]-EDI			
	[Co-Ga-P-O]-EDI			
	|Li-|[Al-Si-O]-EDI			
	$\lvert Rb_7\ Na\ (H_2O)_3\rvert$ $[Ga_8Si_{12}O_{40}]$-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

Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	AlPO-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			
	$\lvert(C_3H_{12}N_2)_4\rvert$ $[Be_8P_8O_{32}]$-GIS			
	$\lvert(C_3H_{12}N_2)_4\rvert$ $[Zn_8P_8O_{32}]$-GIS			
	[Co-Al-P-O]-GIS			
	[Co-Ga-P-O]-GIS			
	[Co-P-O]-GIS			
	$\lvert Cs_4\rvert[Zn_4B_4P_8O_{32}]$-GIS			
	[Ga-Si-O]-GIS			
	[Mg-Al-P-O]-GIS			
	$\lvert(NH_4)_4\rvert[Zn_4B_4P_8O_{32}]$-GIS			
	$\lvert Rb_4\rvert[Zn_4B_4P_8O_{32}]$-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			

Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	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
LEV	*Levyne	2D	3.6 x 4.8	Ring sizes - 8, 6, 4
	AlPO-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,	Ring sizes - 8, 4

Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
			3.3 x 3.3	
	[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			
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			

Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	[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			
	|Rb-|[Be-As-O]-RHO			
	Gallo silicate 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			

Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic framework structures	Dimensionality	Pore size (Å)	Additional info
	[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
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			

[0043] Small pore zeolites with particular application for treating NO_x in exhaust gases of lean-burn internal combustion engines, e.g. vehicular exhaust gases are set out in Table 2.

Table 2: Preferred small pore zeolites, some for use in treating exhaust gases of lean-burn internal combustion engines.

Structure	Zeolite
CHA	SAPO-34
	AlPO-34
	SSZ-13
LEV	Levynite
	Nu-3
	LZ-132
	SAPO-35
	ZK-20
ERI	Erionite
	ZSM-34

Structure	Zeolite
	Linde type T
DDR	Deca-dodecasil 3R
	Sigma-1
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

[0044] Small pore aluminosilicate zeolites for use in the present invention can 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. Therefore, in selecting preferred materials consideration can be given to SAR so that a balance may be struck between these two properties.

[0045] The gas containing the nitrogen oxides can contact the zeolite 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}.

[0046] In one embodiment, the small pore zeolites for use in the present invention do not include aluminophosphate zeolites as defined herein. In a further embodiment, the small pore zeolites (as defined herein) for use in the present invention are restricted to aluminophosphate zeolites (as defined herein). In a further embodiment, small pore zeolites for use in the present invention are aluminosilicate zeolites and metal substituted aluminosilicate zeolites (and not aluminophosphate zeolites as defined herein).

[0047] AEI zeolites for use in the invention have three-dimensional dimensionality, i.e. a pore structure which is interconnected in all three crystallographic dimensions.

[0048] The total of the at least one transition metal included in the at least one transition metal-containing zeolite is from 0.5 to 5wt%.

[0049] The at least one transition metal can be included in the zeolite by any feasible method. For example, it can be added after the zeolite has been synthesised, e.g. by incipient wetness or exchange process; or the at least one metal can be added during zeolite synthesis.

[0050] The zeolite catalyst for use in the present invention can be formed into an extruded-type flow through catalyst.

[0051] Compositions containing the zeolites for use in the present invention for manufacturing extruded type substrate monoliths can comprise a binder selected from the group consisting of alumina, silica, (non-zeolite) silica-alumina, naturally occurring clays, TiO_2, ZrO_2, and SnO_2.

[0052] The nitrogen oxides can be reduced with the reducing agent at a temperature of at least 100°C, such as from about 150°C to 750°C. The latter temperature range is particularly useful for treating exhaust gases from heavy and light duty diesel engines, particularly engines comprising exhaust systems comprising (optionally catalysed) diesel particulate filters which are regenerated actively, e.g. by injecting hydrocarbon into the exhaust system upstream of the filter, wherein the zeolite catalyst for use in the present invention is located downstream of the filter.

[0053] Alternatively, the temperature range is from 175 to 550°C or from 175 to 400°C.

[0054] AEI zeolites for use in the present application are synthetic zeolites, which is advantageous because the zeolites can have a more uniform: silica-to-alumina ratio (SAR), crystallite size, crystallite morphology, and the absence of impurities (e.g. alkaline earth metals).

[0055] The source of nitrogenous reductant can be ammonia *per se,* hydrazine or any suitable ammonia precursor, such as urea ($(NH_2)_2CO$), ammonium carbonate, ammonium carbamate, ammonium hydrogen carbonate or ammonium formate.

[0056] A flow-through monolith substrate as defined herein is a honeycomb monolithic catalyst support structure with many small, parallel channels running axially through the entire part.

[0057] The system can include means, when in use, for controlling the metering means so that nitrogenous reductant is metered into the flowing exhaust gas only when it is determined that the zeolite catalyst is capable of catalysing NO_x reduction at or above a desired efficiency, such as at 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 engine, the position of the exhaust gas recirculation (EGR) valve and thereby the amount of EGR and boost pressure.

[0058] In a particular embodiment, metering is 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 one or more of the abovementioned inputs indicative of a condition of the engine with predicted NO_x content of the exhaust gas.

[0059] The control means can comprise a pre-programmed processor such as an electronic control unit (ECU).

[0060] The metering of the nitrogenous reductant can be arranged such that 60% to 200% of theoretical ammonia is present in exhaust gas entering the SCR catalyst calculated at 1:1 NH_3/NO and 4:3 NH_3/NO_2.

[0061] The system according to the invention comprises an oxidation catalyst for oxidising nitrogen monoxide in the exhaust gas to nitrogen dioxide located upstream of a point of metering the nitrogenous reductant into the exhaust gas. In one embodiment, the oxidation catalyst is adapted to yield a gas stream entering the SCR zeolite catalyst having a ratio of NO to NO_2 of from about 4:1 to about 1:3 by volume, e.g. at an exhaust gas temperature at oxidation catalyst inlet of 250°C to 450°C. This concept is disclosed in S. Kasaoka et al. "Effect of Inlet NO/NO2 Molar Ratio and Contribution of Oxygen in the Catalytic Reduction of Nitrogen Oxides with Ammonia", Nippon Kagaku Kaishi, 1978, No. 6, pp. 874-881 and WO 99/39809.

[0062] The oxidation catalyst includes at least one platinum group metal (or some combination of these), such as platinum, palladium or rhodium, coated on a flow-through monolith substrate. In one embodiment, the at least one platinum group metal is platinum, palladium or a combination of both platinum and palladium. The platinum group metal can be supported on a high surface area washcoat component such as alumina, a zeolite such as an alumino silicate zeolite, silica, non-zeolite silica alumina, ceria, zirconia, titania or a mixed or composite oxide containing both ceria and zirconia.

[0063] In a further embodiment, a suitable filter substrate is located between the oxidation catalyst and the zeolite catalyst. Filter substrates can be selected from any of those mentioned above, e.g. wall flow filters. Where the filter is catalysed, e.g. with an oxidation catalyst of the kind discussed above, preferably the point of metering nitrogenous reductant is located between the filter and the zeolite catalyst. Alternatively, if the filter is uncatalysed, the means for metering nitrogenous reductant can be located between the oxidation catalyst and the filter. It will be appreciated that this arrangement is disclosed in WO 99/39809.

[0064] In a further embodiment, the zeolite catalyst for use in the present invention is coated on a filter located downstream of the oxidation catalyst. Where the filter includes the zeolite catalyst for use in the present invention, the point of metering the nitrogenous reductant is preferably located between the oxidation catalyst and the filter.

[0065] In one embodiment, the control means meters nitrogenous reductant into the flowing exhaust gas only when the exhaust gas temperature is at least 100°C, for example only when the exhaust gas temperature is from 150°C to 750°C.

[0066] In a further aspect, there is provided a vehicular lean-burn engine comprising an exhaust system according to the present invention.

[0067] The vehicular lean burn internal combustion engine can be a diesel engine, a lean-burn gasoline engine or an engine powered by liquid petroleum gas or natural gas.

[0068] In order that the invention may be more fully understood, reference is made to the following Examples by way of illustration only and with reference to the accompanying drawings, in which:

Figure 1 is a graph showing NO_x conversion (at a gas hourly space velocity of 30,000 hr^{-1}) comparing transition metal-containing alumino silicate catalysts with a transition metal-containing aluminophosphate/small pore zeolite catalyst (not according to the invention) after relatively moderate lean hydrothermal ageing performed on a laboratory reactor;

Figure 2 is a graph showing N_2O formation in the test shown in Figure 1;

Figure 3 is a graph showing NO_x conversion (at a gas hourly space velocity of 100,000 hr^{-1}) comparing Cu/Beta zeolite and Cu/SAPO-34 catalysts (none according to the invention) with a transition metal-containing aluminophosphate/small pore zeolite catalyst after relatively moderate lean hydrothermal ageing performed on a laboratory reactor;

Figure 4 is a graph showing NO_x conversion (at a gas hourly space velocity of 30,000 hr^{-1}) comparing transition metal-containing alumino silicate catalysts with a transition metal-containing aluminophosphate/small pore zeolite catalyst (not according to the invention) after relatively severe lean hydrothermal ageing performed on a laboratory reactor;

Figure 5 is a graph showing NO_x conversion for fresh Cu/Zeolite catalysts (not according to the invention);

Figure 6 is a graph showing NO_x conversion for aged Cu/Zeolite catalysts (not according to the invention);

Figure 7 is a graph showing N_2O formation for fresh Cu/Zeolite catalysts (not according to the invention) of Figure 5;

Figure 8 is a graph showing N_2O formation for aged Cu/Zeolite catalysts (not according to the invention) of Figure 6;

Figure 9 is a graph showing the effect of adding HC species to Cu/zeolite catalysts (not according to the invention) during NH_3 SCR at 300°C;

Figure 10 is a graph showing hydrocarbon breakthrough following addition of hydrocarbon species to Cu/zeolite catalysts (not according to the invention) during NH_3 SCR at 300°C;

Figure 11 is a graph showing the adsorption profiles of n-octane at 150°C flowing through the Cu zeolite catalysts (not according to the invention);

Figure 12 is a graph of the temperature programmed desorption (TPD) of HC species to Cu/zeolite catalysts (not according to the invention) after HC adsorption at 150°C;

Figure 13 is a graph similar to Figure 6 comparing NO_x conversion activity for aged Cu/Sigma-1, Cu-SAPO-34, Cu/SSZ-13 and Cu/Beta (none according to the invention);

Figure 14 is a graph similar to Figure 8 comparing N_2O formation for the aged Cu/zeolite catalysts (none according to the invention) of Figure 13;

Figure 15 is a graph similar to Figure 13 comparing NO_x conversion activity for aged Cu/ZSM-34, Cu/SAPO-34, Cu/SSZ-13 and Cu/Beta catalysts (none according to the invention);

Figure 16 is a graph comparing the NO_x conversion activity of fresh and aged Cu-SAPO-34 and Cu/SSZ-13 catalysts (not according to the invention);

Figure 17 is a graph comparing the NO_x conversion activity of fresh samples of Cu/SAPO-34 with a Cu/naturally occurring chabazite type material (neither according to the invention);

Figure 18 is a bar chart comparing the NO_x conversion activity of fresh Cu/SAPO-34 with that of two fresh Cu/naturally occurring chabazite type materials (none according to the invention) at two temperature data points;

Figure 19 is a bar chart comparing the NO_x conversion activity of aged Cu/Beta, Cu/SAPO-34, Fe/SAPO-34 and Fe/SSZ-13 catalysts (none according to the invention) at two temperature data points;

Figure 20 is a bar chart comparing the hydrocarbon inhibition effect of introducing n-octane into a feed gas for fresh Fe/Beta and Fe/SSZ-13 catalysts (not according to the invention);

Figure 21 is a graph showing hydrocarbon breakthrough following the introduction of n-octane in the experiment of Figure 20;

Figure 22 is a bar chart comparing the effect on NO_x conversion activity for a fresh Fe/SSZ-13 catalyst (not according to the invention) of using 100% NO as a component of the feed gas with using 1:1 NO:NO_2;

Figure 23 is a schematic diagram of an embodiment of an exhaust system according to the present invention.

[0069] Figure 23 is a schematic diagram of an embodiment of an exhaust system according to the present invention, wherein diesel engine 12 comprises an exhaust system 10 according to the present invention comprising an exhaust line 14 for conveying an exhaust gas from the engine to atmosphere via tailpipe 15. In the flow path of the exhaust gas is disposed a platinum or platinum/palladium NO oxidation catalyst 16 coated on a ceramic flow-through substrate monolith. Located downstream of oxidation catalyst 16 in the exhaust system is a ceramic wall-flow filter 18.

[0070] An iron/small pore zeolite SCR catalyst 20 (not according to the invention) also coated on a ceramic flow-through substrate monolith is disposed downstream of the wall-flow filter 18. An NH_3 oxidation clean-up or slip catalyst 21 is coated on a downstream end of the SCR catalyst monolith substrate. Alternatively, the NH_3 slip catalyst can be coated on a separate substrate located downstream of the SCR catalyst. Means (injector 22) is provided for introducing nitrogenous reductant fluid (urea 26) from reservoir 24 into exhaust gas carried in the exhaust line 14. Injector 22 is controlled using valve 28, which valve is in turn controlled by electronic control unit 30 (valve control represented by dotted line). Electronic control unit 30 receives closed loop feedback control input from a NO_x sensor 32 located downstream of the SCR catalyst.

[0071] In use, the oxidation catalyst 16 passively oxidises NO to NO_2, particulate matter is trapped on filter 18 and is combusted in NO_2. NO_x emitted from the filter is reduced on the SCR catalyst 20 in the presence of ammonia derived from urea injected via injector 22. It is also understood that mixtures of NO and NO_2 in the total NO_x content of the exhaust gas entering the SCR catalyst (about 1:1) are desirable for NO_x reduction on a SCR catalyst as they are more readily reduced to N_2. The NH_3 slip catalyst 21 oxidises NH_3 that would otherwise be exhausted to atmosphere. A similar arrangement is described in WO 99/39809.

EXAMPLES

Example 1 - Method of making fresh 5wt% Fe/Beta or SAPO-34 or 3wt% SSZ-13 zeolite catalyst (not according to the invention)

[0072] Commercially available Beta zeolite, SAPO-34 or SSZ-13 was NH_4^+ ion exchanged in a solution of NH_4NO_3, then filtered. The resulting material was added to an aqueous solution of $Fe(NO_3)_3$ with stirring. The slurry was filtered, then washed and dried. The procedure can be repeated to achieve a desired metal loading. The final product was calcined.

Example 2 - Method of making fresh 3wt% Cu/zeolites

[0073] Commercially available SAPO-34, SSZ-13, Sigma-1, ZSM-34, Nu-3, ZSM-5 and Beta zeolites (none according to the invention) were NH_4^+ ion exchanged in a solution of NH_4NO_3, then filtered. The resulting materials were added to an aqueous solution of $Cu(NO_3)_2$ with stirring. The slurry was filtered, then washed and dried. The procedure can be repeated to achieve a desired metal loading. The final product was calcined.

Example 3 - Lean Hydrothermal Ageing

[0074] The catalysts obtained by means of Examples 1 and 2 were lean hydrothermally aged at 750°C for 24 hours in 4.5% H_2O/air mixture.

Example 4 - Severe Lean Hydrothermal Ageing

[0075] The catalysts obtained by means of Examples 1 and 2 were severely lean hydrothermally aged at 900°C for 1 hour in 4.5% H_2O/air mixture.

Example 5 - Extended Severe Lean Hydrothermal Ageing

[0076] The catalysts obtained by means of Examples 1 and 2 were severely lean hydrothermally aged at 900°C for a period of 3 hours in 4.5% H_2O/air mixture.

Example 6 -Test Conditions

[0077] Separate samples of Fe/Beta prepared according to Example 1 and Cu/Beta, Cu/ZSM-5 and Cu/SAPO-34 (none according to the invention) prepared according to Example 2 were aged according to Examples 3 and 4 and tested in a laboratory apparatus using the following gas mixture: 350ppm NO, 350ppm NH_3, 14%O_2, 4.5% H_2O, 4.5% CO_2, N_2 balance. The results are shown in Figures 1 to 4 inclusive.

[0078] Tests were also conducted on Cu/Beta, Cu/ZSM-5, Cu/SAPO-34 and Cu/Nu-3 (none according to the invention) prepared according to Example 2 and aged according to Example 3 and tested in a laboratory apparatus using the same gas mixture as described above, except in that 12%O_2 was used. The results are shown in Figures 5 to 8 inclusive.

Example 7 - n-Octane adsorption test conditions

[0079] With the catalyst loaded in a laboratory apparatus, 1000ppm (as C1 equivalents) propene, n-octane or toluene was injected during NH_3 SCR at 300°C (350ppm NO, 350ppm NH_3, 12%O_2, 4.5%H_2O, 4.5%CO_2, balance N_2). Hydrocarbon desorption was measured by ramping the temperature at 10°C/minute in 12%O_2, 4.5%H_2O, 4.5%CO_2, balance N_2.

Example 8 - Results for experiments shown in Figures 1 to 4 inclusive (not according to the invention)

[0080] Figure 1 compares the NO_x reduction efficiencies of a Cu/SAPO-34 catalyst against a series of aluminosilicate zeolite supported transition metal catalysts (Cu/ZSM-5, Cu/Beta and Fe/Beta) after a mild aging. The result clearly demonstrates that Cu/SAPO-34 has improved low temperature activity for SCR of NO_x with NH_3.

[0081] Figure 2 compares the N_2O formation over the catalysts. It is clear that the Cu/SAPO-34 catalyst produced lower levels of N_2O compared to the other two Cu-containing catalysts. The Fe-containing catalyst also exhibits low N_2O formation, but as shown in Figure 1, the Fe catalyst is less active at lower temperatures.

[0082] Figure 3 compares the NO_x reduction efficiencies of a Cu/SAPO-34 catalyst against a Cu/Beta catalyst tested at a higher gas hourly space velocity. The Cu/SAPO-34 catalyst is significantly more active than the Cu-Beta catalyst at low reaction temperatures.

[0083] Figure 4 shows the NO_x reduction efficiencies of a Cu/SAPO-34 catalyst and a series of aluminosilicate zeolite supported transition metal catalysts (Cu/ZSM-5, Cu/Beta, and Fe/Beta) after severe lean hydrothermal aging. The result clearly demonstrates that the Cu/SAPO-34 catalyst has superior hydrothermal stability.

Example 9 - Results for experiments shown in Figures 5 to 12 inclusive (not according to the invention)

[0084] NH_3 SCR activity of fresh (i.e. un-aged) Cu supported on the small pore zeolites SAPO-34 and Nu-3 was compared to that of Cu supported on larger pore zeolites in Figure 5. The corresponding activity for the same catalysts aged under severe lean hydrothermal conditions is shown in Figure 6. Comparison of the fresh and aged activity profiles demonstrates that hydrothermal stability is only achieved for aluminosilicate zeolites when the Cu is supported on a small pore zeolite.

[0085] The N_2O formation measured for the fresh and aged catalysts is shown in Figures 7 and 8, respectively. The results clearly show that N_2O formation is significantly reduced by

means of supporting Cu on zeolites that do not have large pores.

[0086] Figure 9 compares the effect of HC on Cu/zeolite catalysts where SAPO-34 and Nu-3 are used as examples of small pore zeolite materials. For comparison, ZSM-5 and Beta zeolite are used as examples of a medium and large pore zeolite, respectively. Samples were exposed to different HC species (propene, n-octane and toluene) during NH_3 SCR reaction at 300°C. Figure 10 shows the corresponding HC breakthrough following HC addition.

[0087] Figure 11 shows the adsorption profiles of n-octane at 150°C flowing through different Cu/zeolite catalysts. HC breakthrough is observed almost immediately with Cu supported on the small pore zeolites SAPO-34 and Nu-3, whereas significant HC uptake is observed with Cu on Beta zeolite and ZSM-5. Figure 12 shows the subsequent HC desorption profile as a function of increasing temperature and confirms that large amounts of HC are stored when Cu is supported on the larger pore zeolites, whereas very little HC is stored when small pore zeolites are employed.

Example 10 - Results for experiments shown in Figures 13 and 14 (not according to the invention)

[0088] Cu/SSZ-13, Cu/SAPO-34, Cu/Sigma-1 and Cu/Beta prepared according to Example 2 were aged in the manner described in Example 4 and tested according to Example 6. The results are shown in Figure 13, from which it can be seen that the NO_x conversion activity of each of the severely lean hydrothermally aged Cu/SSZ-13, Cu/SAPO-34 and Cu/Sigma-1 samples is significantly better than that of the corresponding large-pore zeolite, Cu/Beta. Moreover, from Figure 14 it can be seen that Cu/Beta generates significantly more N_2O than the Cu/small-pore zeolite catalysts.

Example 11 - Results for experiments shown in Figure 15 (not according to the invention)

[0089] Cu/ZSM-34, Cu/SAPO-34, Cu/SSZ-13 and Cu/Beta prepared according to Example 2 were aged in the manner described in Example 3 and tested according to Example 6. The results are shown in Figure 15, from which it can be seen that the NO_x conversion activity of each of the lean hydrothermally aged Cu/SSZ-13, Cu/SAPO-34 and Cu/ZSM-34 samples is significantly better than that of the corresponding large-pore zeolite, Cu/Beta.

Example 12 - Results for experiments shown in Figure 16 (not according to the invention)

[0090] Fresh samples of Cu/SSZ-13 and Cu/SAPO-34 were prepared according to Example 2, samples of which were aged in the manner described in Example 5. Fresh (i.e. un-aged) and aged samples were tested according to Example 6 and the results are shown in Figure 16, from which it can be seen that the NO_X conversion activity of Cu/SSZ-13 is maintained even after extended severe lean hydrothermal ageing.

Example 13 - Results for experiments shown in Figures 17 and 18 (not according to the invention)

[0091] Cu/SAPO-34 and a Cu/naturally occurring chabazite type material having a SAR of about 4 were prepared according to Example 2 and the fresh materials were tested according to Example 6. The results are shown in Figure 17, from which it can be seen that the NO_X conversion activity of the naturally occurring Cu/chabazite is significantly lower than Cu/SAPO-34. Figure 18 is a bar chart comparing the NO_X conversion activity of two fresh Cu/naturally occurring chabazite type materials prepared according to Example 2 at two temperature data points (200°C and 300°C), a first chabazite material having a SAR of about 4 and a second chabazite material of SAR about 7. It can be seen that whilst the NO_X conversion activity for the SAR 7 chabazite is better than for the SAR 4 chabazite material, the activity of the SAR 7 chabazite material is still significantly lower than the fresh Cu/SAPO-34.

Example 14 - Results for experiments shown in Figure 19 (not according to the invention)

[0092] Cu/SAPO-34 and Cu/Beta were prepared according to Example 2. Fe/SAPO-34 and Fe/SSZ-13 were prepared according to Example 1. The samples were aged according to Example 4 and the aged samples were tested according to Example 6. The NO_X activity at the 350°C and 450°C data points is shown in Figure 19, from which it can be seen that the Cu/SAPO-34, Fe/SAPO-34 and Fe/SSZ-13 samples exhibit comparable or better performance than the Cu/Beta reference.

Example 15 - Results for experiments shown in Figures 20 and 21 (not according to the invention)

[0093] Fe/SSZ-13 and Fe/Beta prepared according to Example 1 were tested fresh as described in Example 7, wherein n-octane (to replicate the effects of unburned diesel fuel in an exhaust gas) was introduced at 8 minutes into the test. The results shown in Figure 20 compare the NOx conversion activity at 8 minutes into the test, but before n-octane was introduced into the feed gas (HC-) and 8 minutes after n-octane was introduced into the feed gas (HC+). It can be seen that the Fe/Beta activity dramatically reduces following n-octane

introduction compared with Fe/SSZ-13. We believe that this effect results from coking of the catalyst.

[0094] The hypothesis that coking of the Fe/Beta catalyst is responsible for the dramatic reduction of NO_x conversion activity is reinforced by the results shown in Figure 21, wherein C1 hydrocarbon is detected downstream of the Fe/SSZ-13 catalyst almost immediately after n-octane is introduced into the feed gas at 8 minutes. By comparison, a significantly lower quantity of C1 hydrocarbon is observed in the effluent for the Fe/Beta sample. Since there is significantly less C1 hydrocarbon present in the effluent for the Fe/Beta sample, and the n-octane must have gone somewhere, the results suggest that it has become coked on the Fe/Beta catalyst, contributing to the loss in NO_x conversion activity.

Example 16 - Results for experiments shown in Figure 22 (not according to the invention)

[0095] Fe/SSZ-13 prepared according to Example 1 was tested fresh, i.e. without ageing, in the manner described in Example 6. The test was then repeated using identical conditions, except in that the 350ppm NO was replaced with a mixture of 175ppm NO and 175ppm NO_2, i.e. 350ppm total NO_x. The results from both tests are shown in Figure 22, from which the significant improvement obtainable from increasing the NO_2 content of NO_x in the feed gas to 1:1 can be seen. In practice, the NO:NO_2 ratio can be adjusted by oxidising NO in an exhaust gas, e.g. of a diesel engine, using a suitable oxidation catalyst located upstream of the NH_3-SCR catalyst.

REFERENCES CITED IN THE DESCRIPTION

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- US6514470B [0015]
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- **LONG et al.**Journal of Catalysis, 2002, vol. 207, 274-285 [0016] [0031]
- **S. KASAOKA et al.**Effect of Inlet NO/NO2 Molar Ratio and Contribution of Oxygen in the Catalytic Reduction of Nitrogen Oxides with AmmoniaNippon Kagaku Kaishi, 1978, vol. 6, 874-881 [0061]

Patentkrav

1. Udstødningssystem til en forbrændingsmotor med mager forbrænding til køretøjer, hvilket system omfatter en ledning til at transportere en strømmende udstødningsgas, en kilde til nitrogenholdigt reduktionsmiddel, en katalysator af ekstruderet type, der er dannet fra en zeolit-katalysator, som er anbragt i en strømningsvej for en udstødningsgas, midler til at dosere nitrogenholdigt reduktionsmiddel ind i en strømmende udstødningsgas opstrøms for katalysatoren af ekstruderet type og en oxidationskatalysator, der omfatter mindst et metal fra platingruppen til oxidation af nitrogenmonoxid til nitrogendioxid, der er til stede opstrøms for midlerne til at dosere nitrogenholdigt reduktionsmiddel ind i en strømmende udstødningsgas gas, hvilken zeolitkatalysator er en zeolit, der har små porer, og som indeholder en maksimal ringstørrelse på otte tetraederiske atomer og som har AEI-Framework-Type-Code, og hvor det totale indhold af det mindst ene overgangsmetal, der er til stede i katalysatoren, er på fra 0,5 til 5 vægt % baseret på den totale vægt af zeolitkatalysatoren, hvilket mindst ene overgangsmetal er kobber.

2. Udstødningssystemet ifølge krav 1, hvor zeolitten, der har små porer, er valgt fra gruppen, der består af aluminosilicatzeolitter, metalsubstituerede aluminosilicatzeolitter og aluminophosphatzeolitter.

3. Udstødningssystemet ifølge krav 2, hvor zeolitten, der har små porer, er en aluminosilicatzeolit og har et forhold mellem siliciumdioxid og aluminiumoxid (SAR) på 2 til 300.

4. Udstødningssystemet ifølge krav 3, hvor SAR er på 8 til 150.

5. Udstødningssystem ifølge et hvilket som helst af de foregående krav, hvor zeolitten, der har små porer, er AlPO-18 eller er en isotype, der har AEI-Framework-Type-Code valgt fra gruppen, der består af [Co-Al-PO]-AEI, SAPO-18, SIZ- 8 og SSZ-39.

6. Udstødningssystem ifølge et hvilket som helst af de foregående krav, hvor kobberet er blevet tilsat ved ionbytning, imprægnering eller isomorf substitution til zeolitstrukturen, der har små porer.

7. Udstødningssystemet ifølge krav 6, hvor kobberet er blevet tilsat ved ionbytning.

8. Udstødningssystem ifølge et hvilket som helst af de foregående krav i form af en substratmonolit, der omfatter en kombination af to eller flere overgangsmetalholdige zeolitter, der har små porer.

9. Udstødningssystem ifølge et hvilket som helst af de foregående krav, hvor katalysatoren af ekstruderet type er i form af en substratmonolit, der omfatter mindst et bindemiddel, som er udvalgt fra gruppen, der består af aluminiumoxid, siliciumdioxid, ikke-zeolit-siliciumdioxid-aluminiumoxid, en naturligt forekommende ler, TiO_2, ZrO_2 og SnO_2.

10. Udstødningssystem ifølge et hvilket som helst af de foregående krav, hvor katalysatoren af ekstruderet type er en gennemstrømningskatalysator af ekstruderet type.

11. Udstødningssystem ifølge krav 1, hvor et filtersubstrat er anbragt mellem oxidationskatalysatoren og katalysatoren af ekstruderet type.

12. Forbrændingsmotor med mager forbrænding til køretøjer, hvilken forbrændingsmotor omfatter et udstødningssystem ifølge et hvilket som helst af de foregående krav.

DRAWINGS

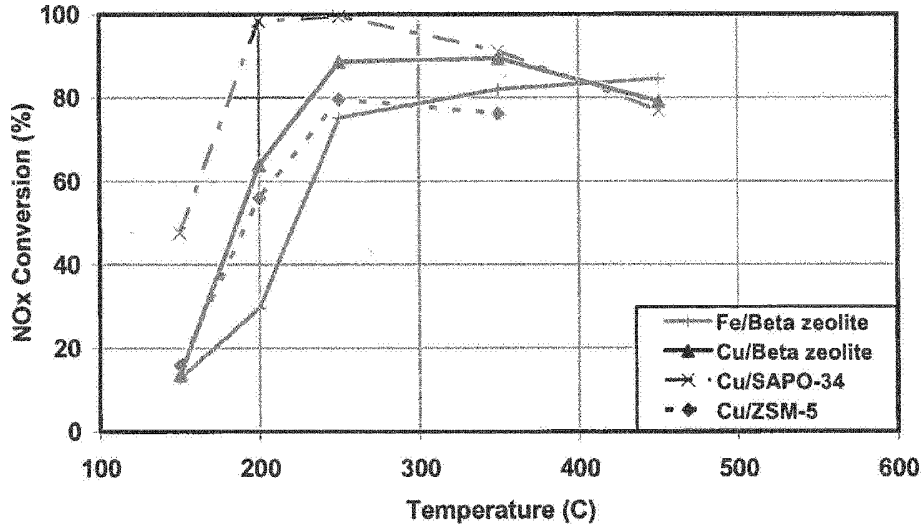


FIGURE 1

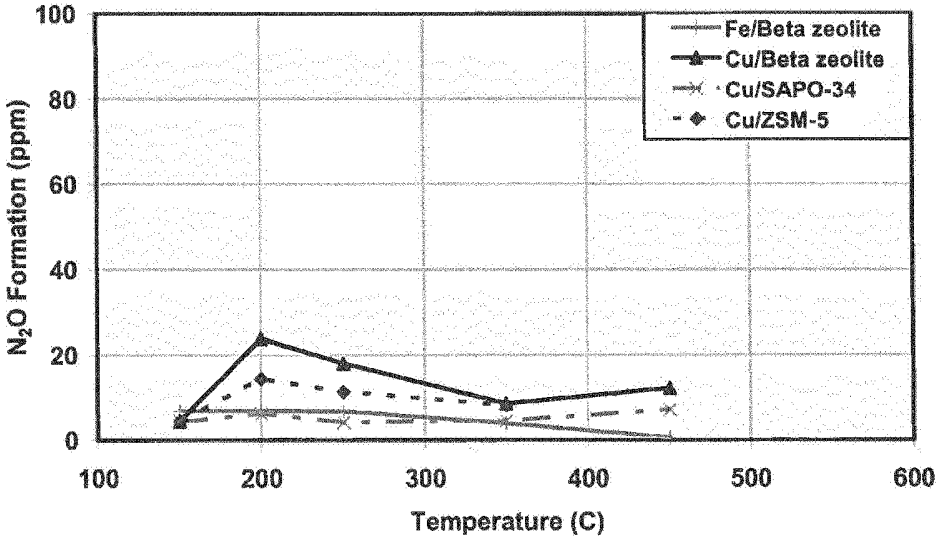
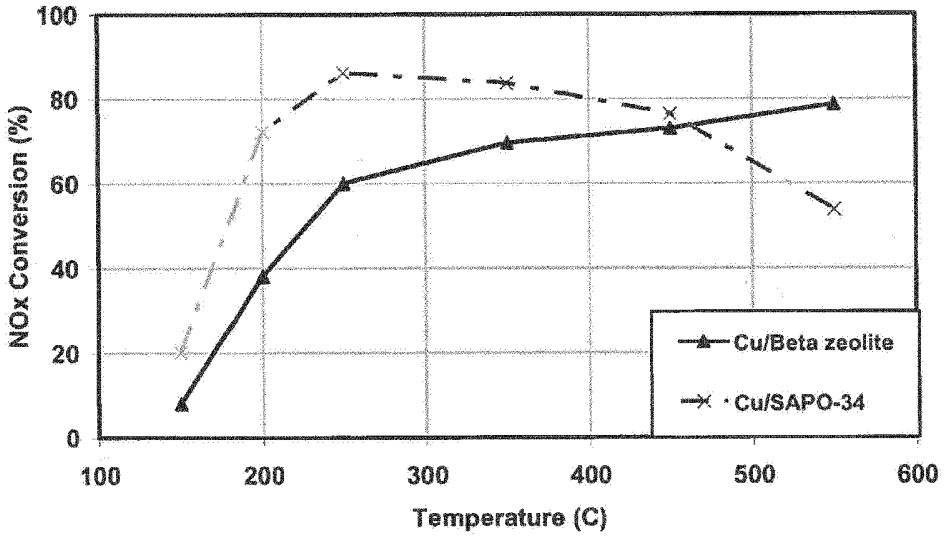


FIGURE 2



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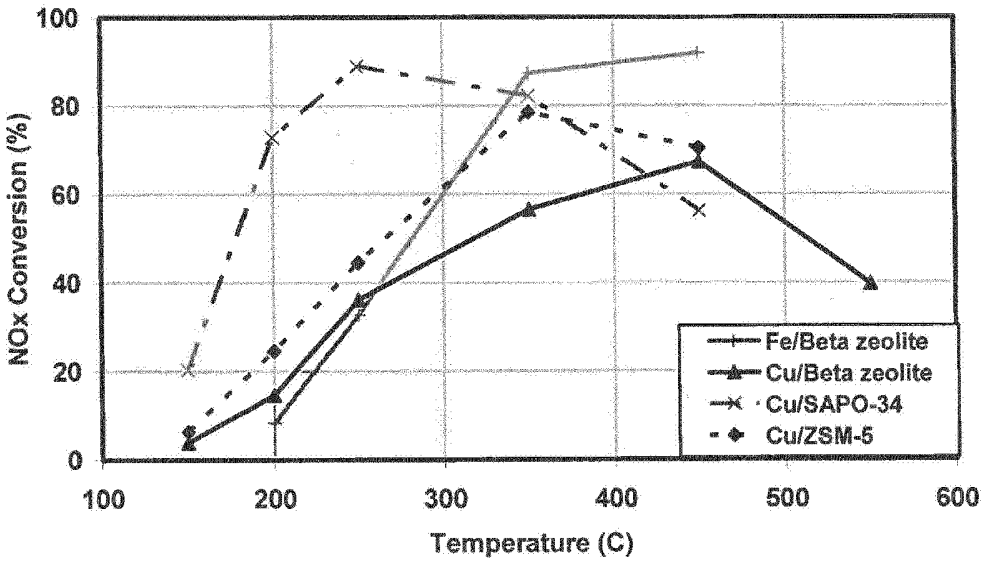

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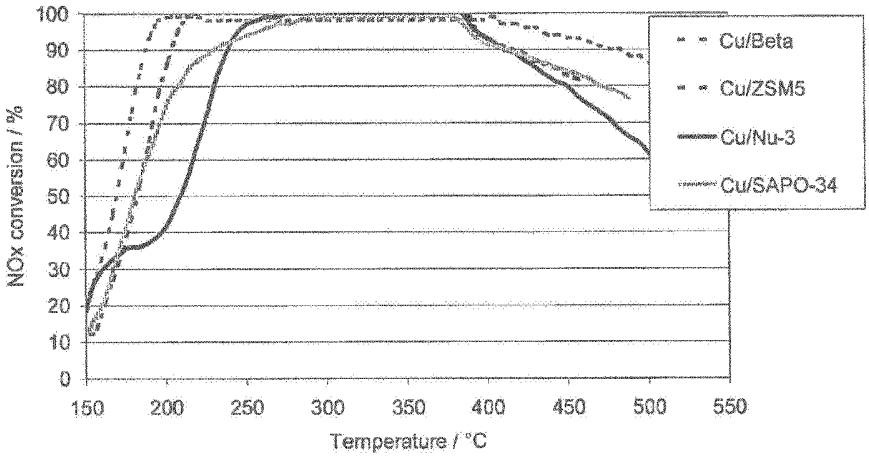

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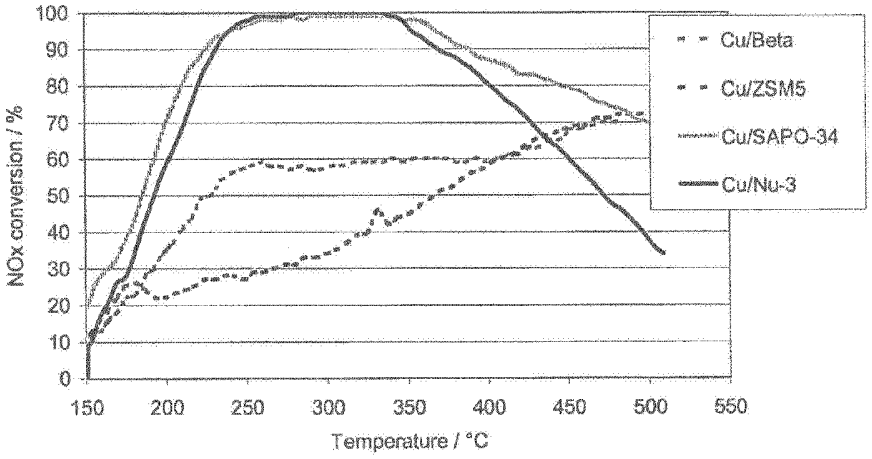

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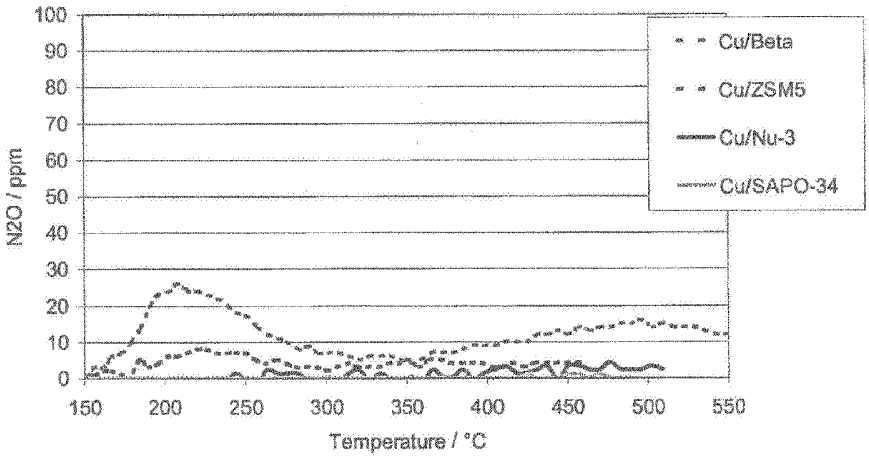

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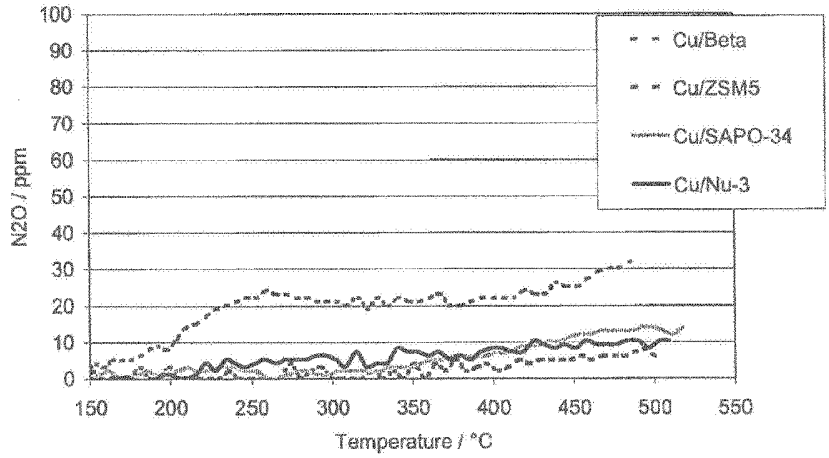


FIGURE 8

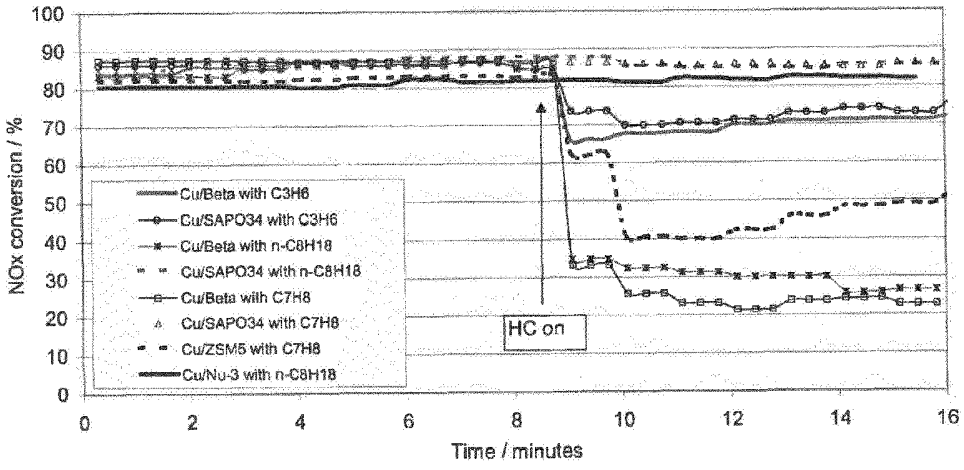


FIGURE 9

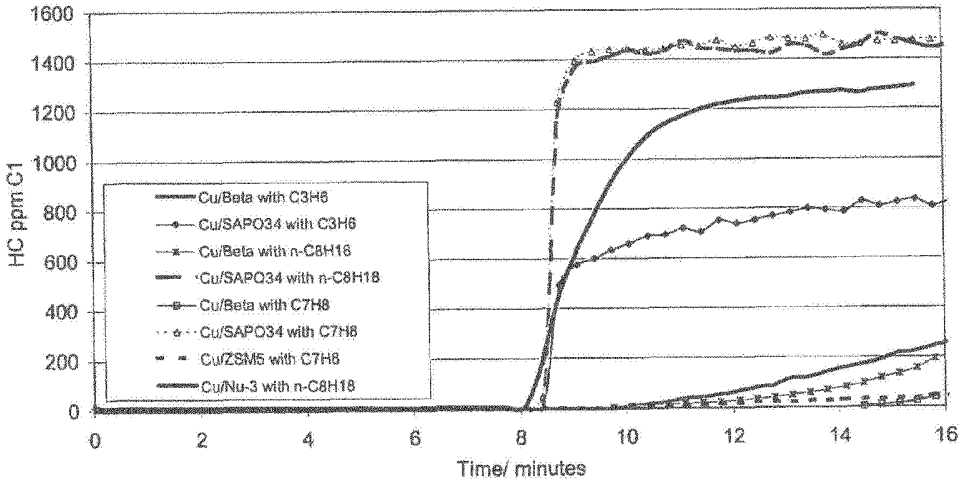
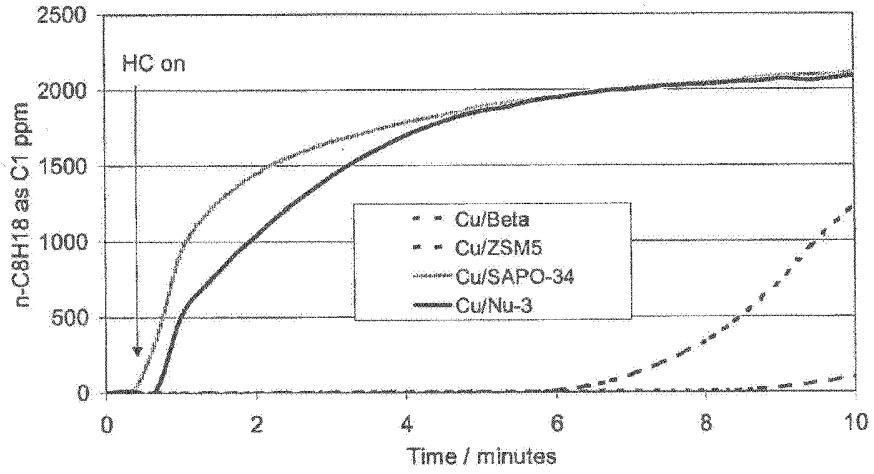


FIGURE 10



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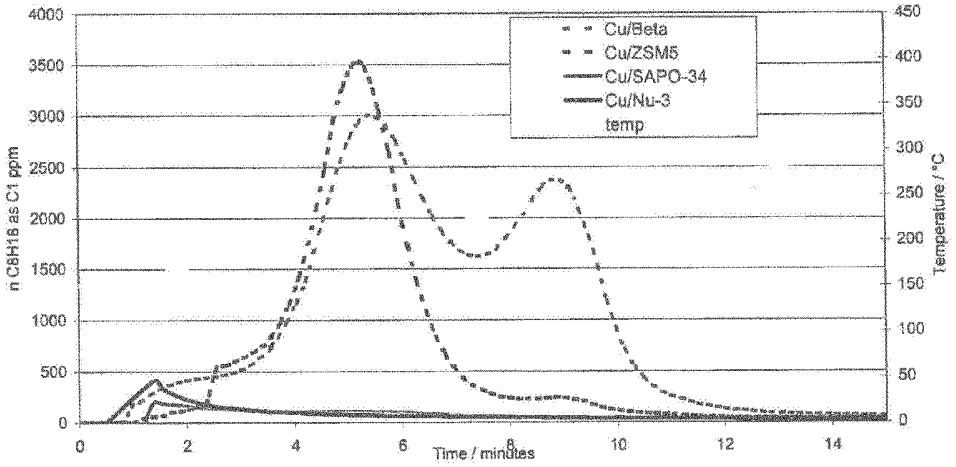


FIGURE 12

Figure 13

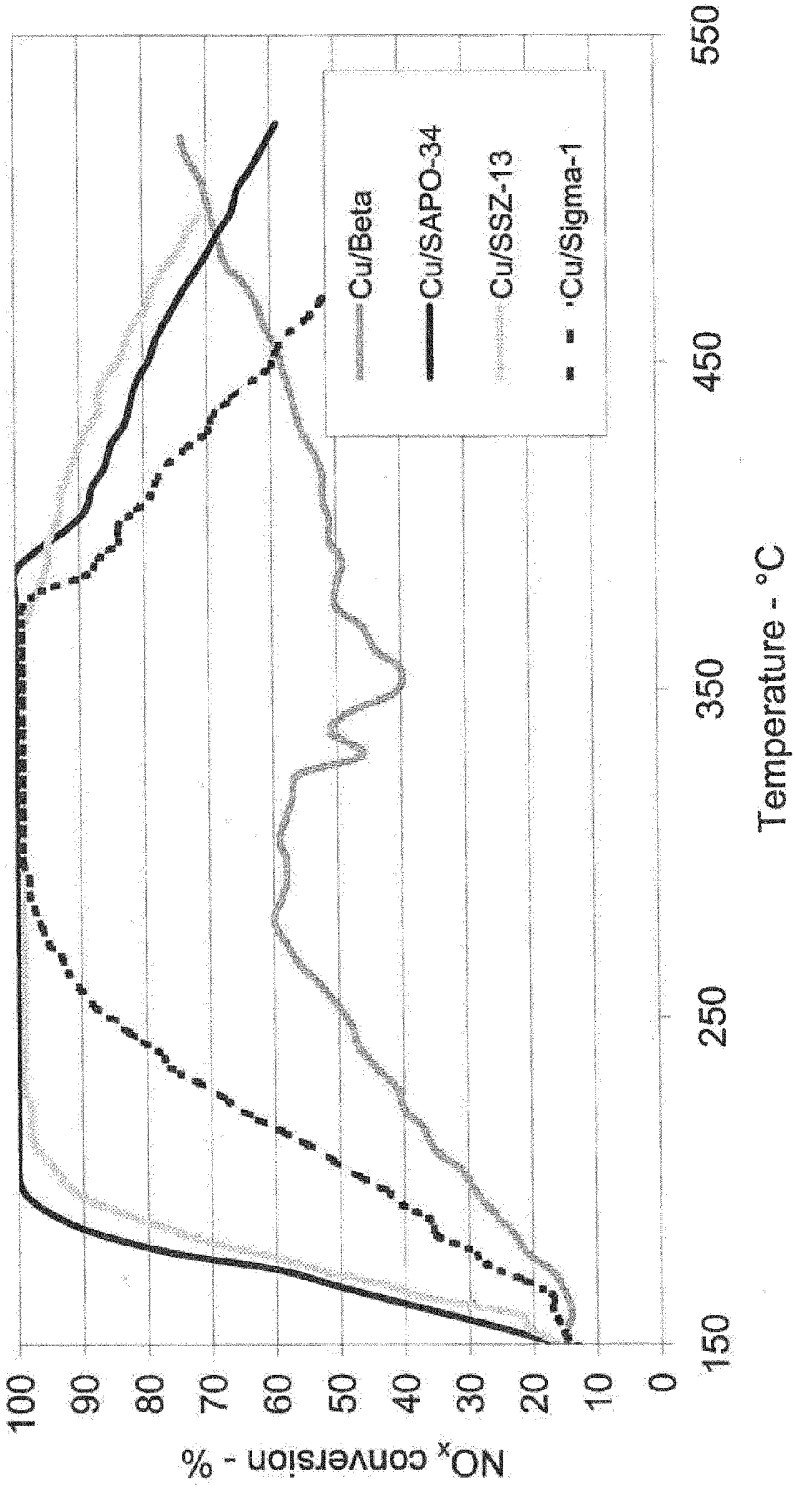

NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
150
250
350
450
550
Temperature - °C
Cu/Beta
Cu/SAPO-34
Cu/SSZ-13
'Cu/Sigma-1

Figure 14

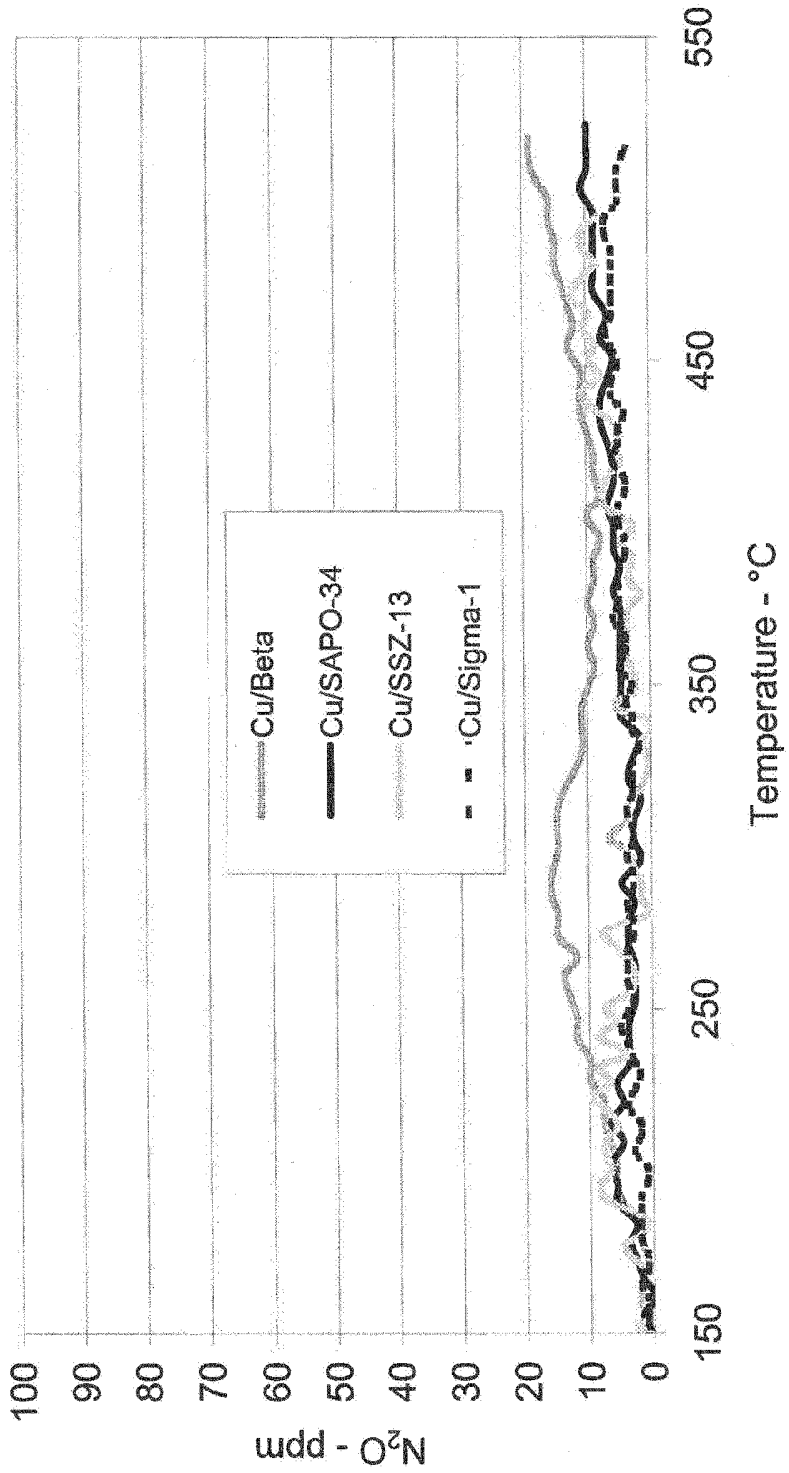

Cu/Beta
Cu/SAPO-34
Cu/SSZ-13
Cu/Sigma-1
N2O - ppm
Temperature - °C
0
10
20
30
40
50
60
70
80
90
100
150
250
350
450
550

Figure 15

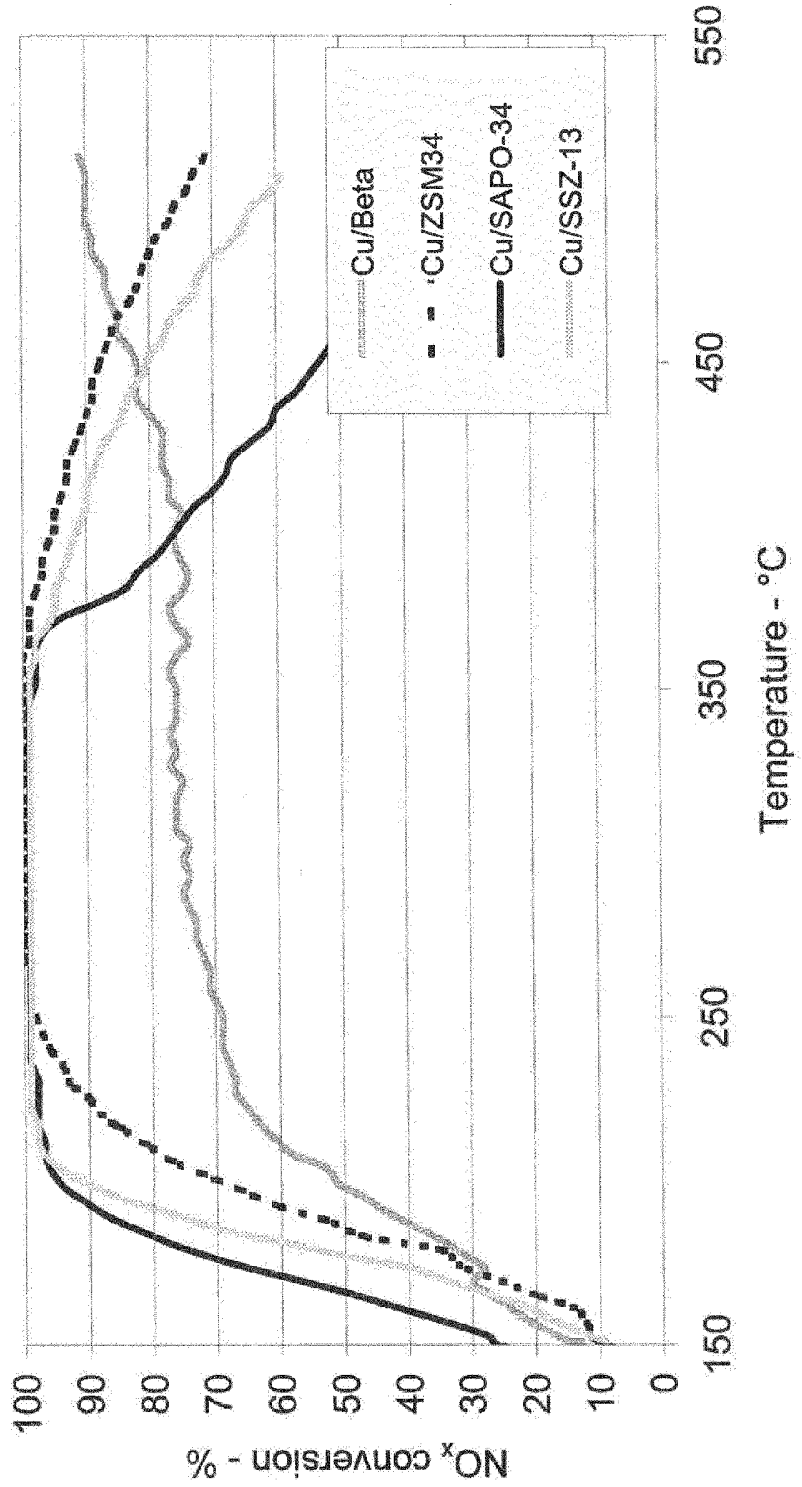

NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
150
250
350
450
550
Temperature - °C
Cu/Beta
Cu/ZSM34
Cu/SAPO-34
Cu/SSZ-13

Figure 1b

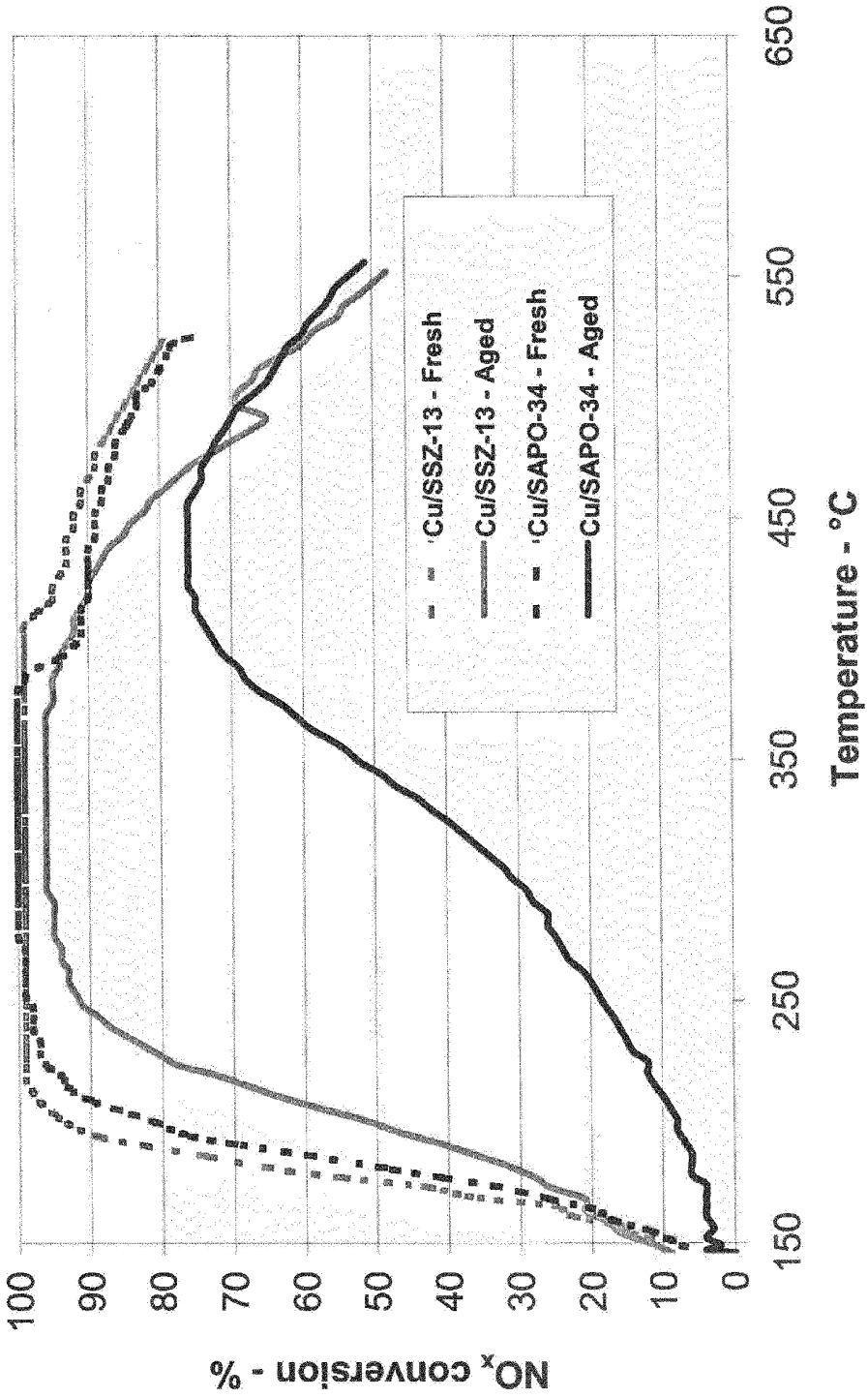

NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
150
250
350
450
550
650
Temperature - °C
Cu/SSZ-13 - Fresh
Cu/SSZ-13 - Aged
Cu/SAPO-34 - Fresh
Cu/SAPO-34 - Aged

Figure 17

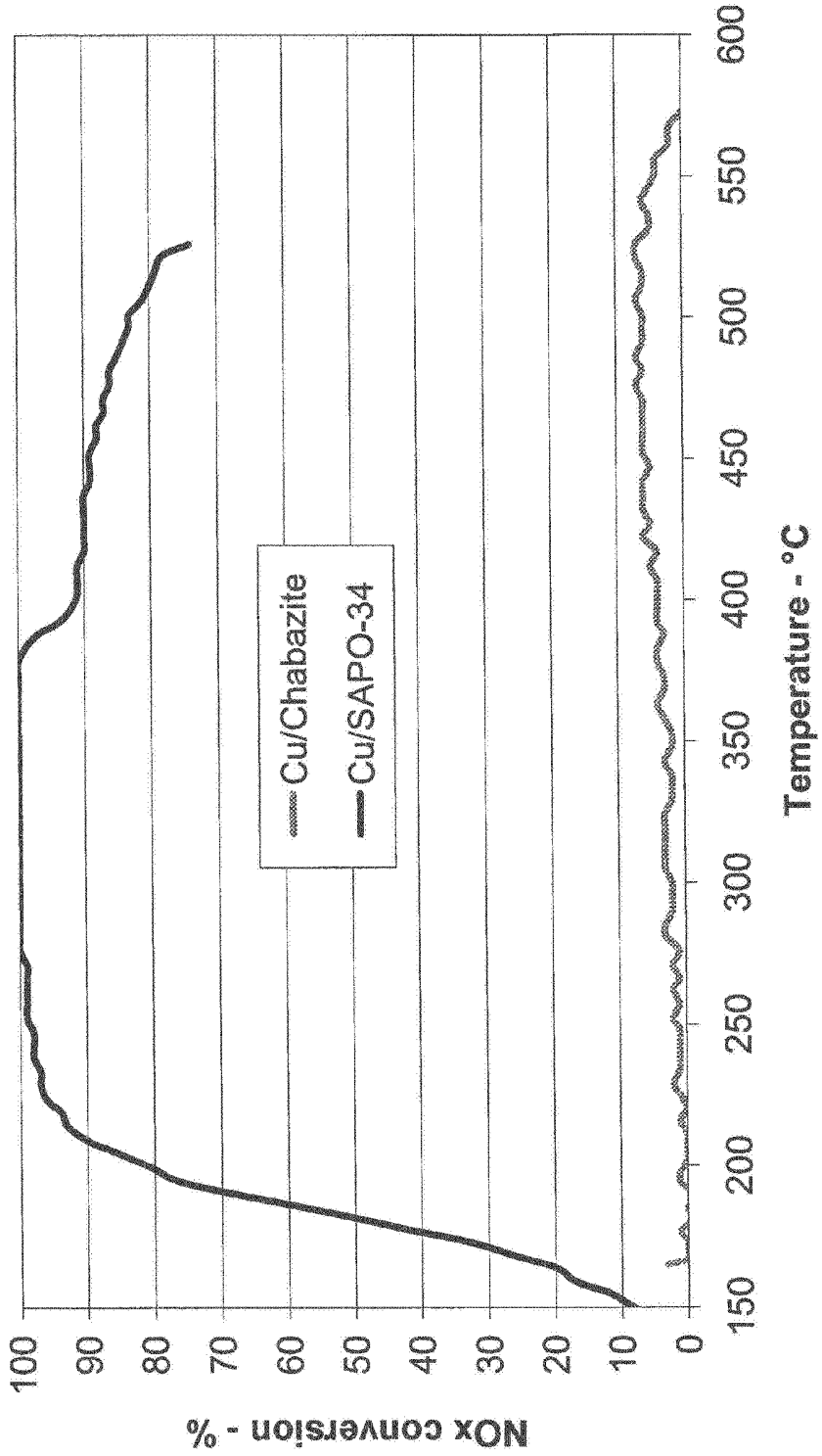

NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
150
200
250
300
350
400
450
500
550
600
Temperature - °C
Cu/Chabazite
Cu/SAPO-34

Figure 12

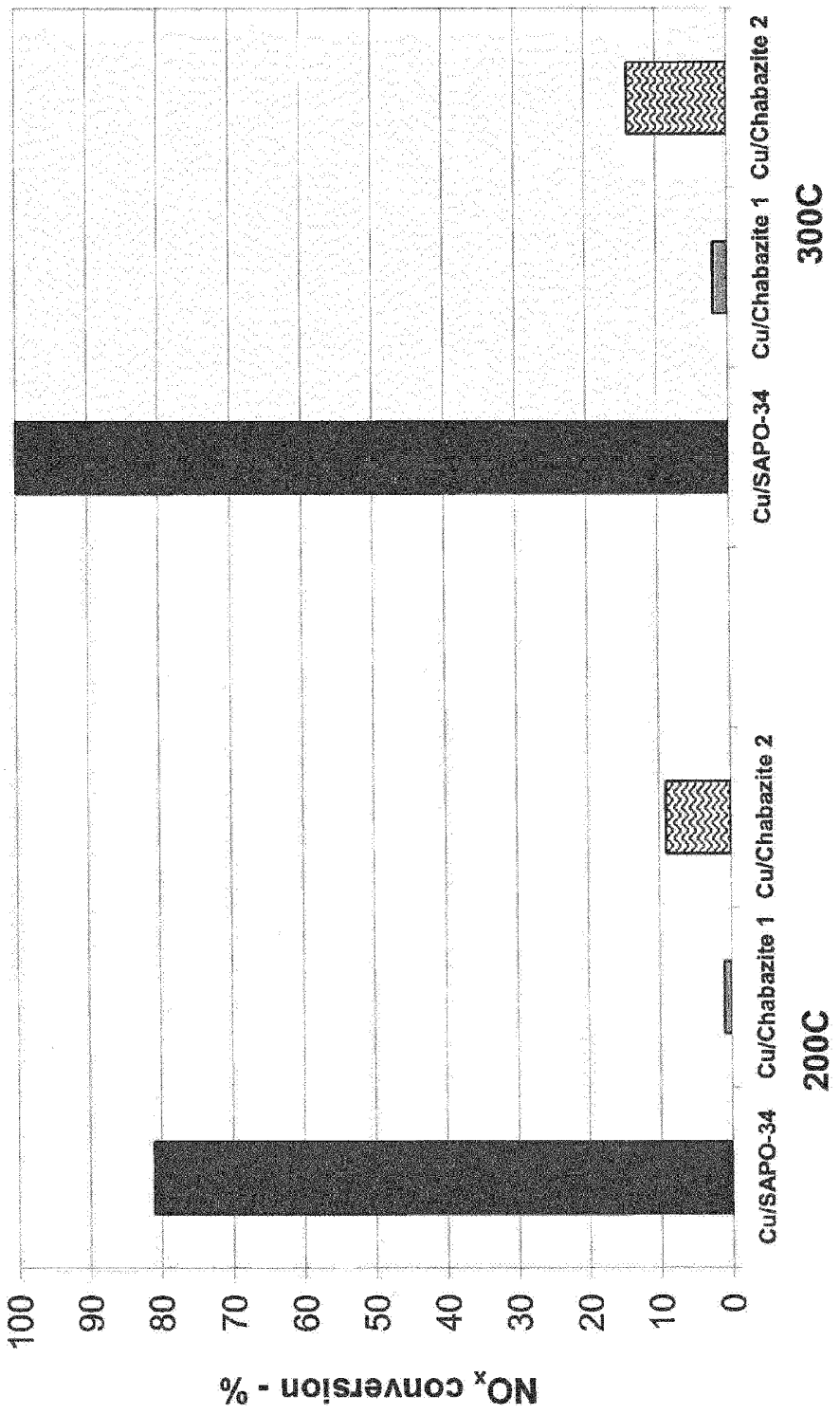

NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
Cu/SAPO-34
Cu/Chabazite 1
Cu/Chabazite 2
200C
Cu/SAPO-34
Cu/Chabazite 1
Cu/Chabazite 2
300C

Figure 19

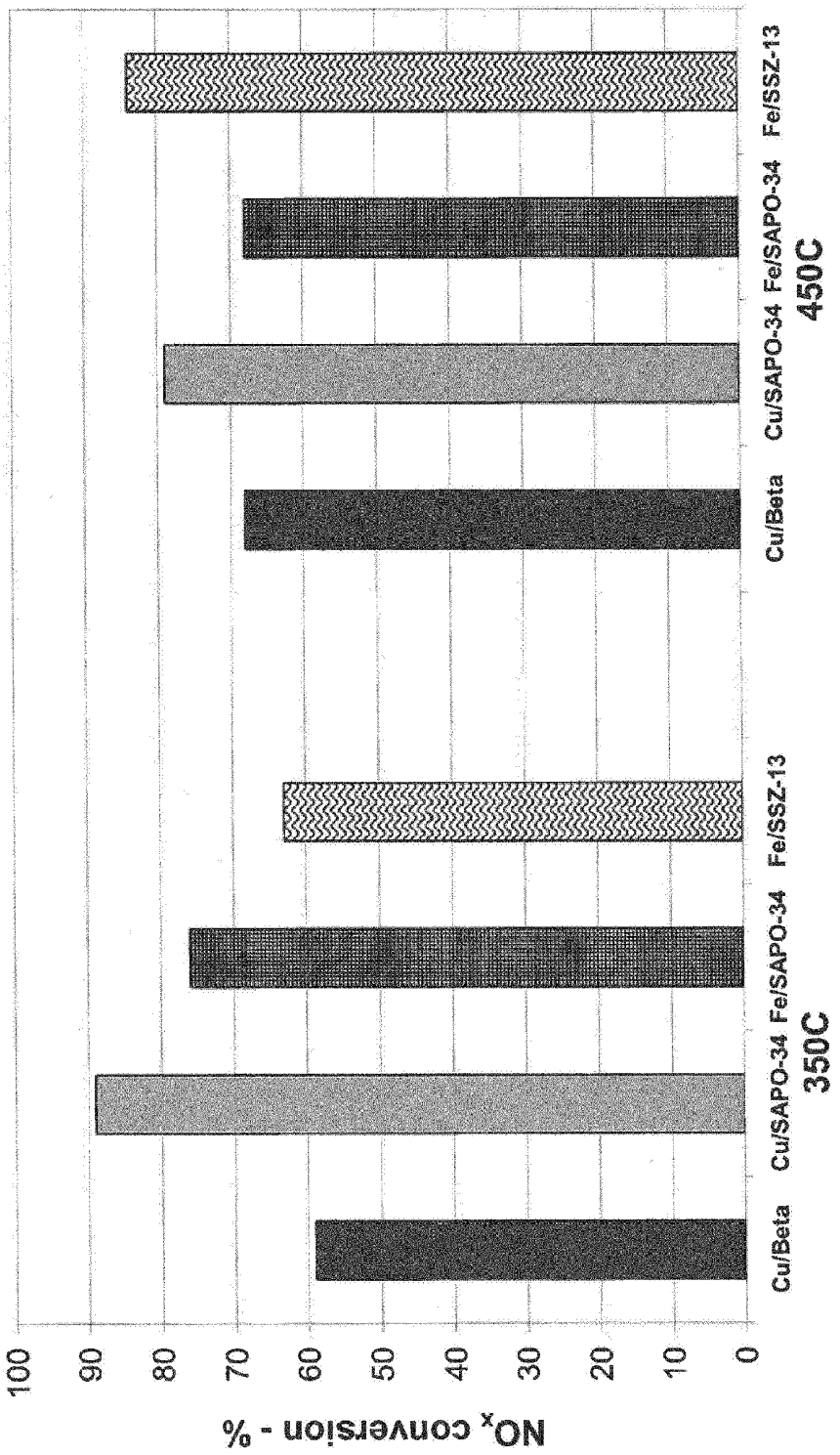
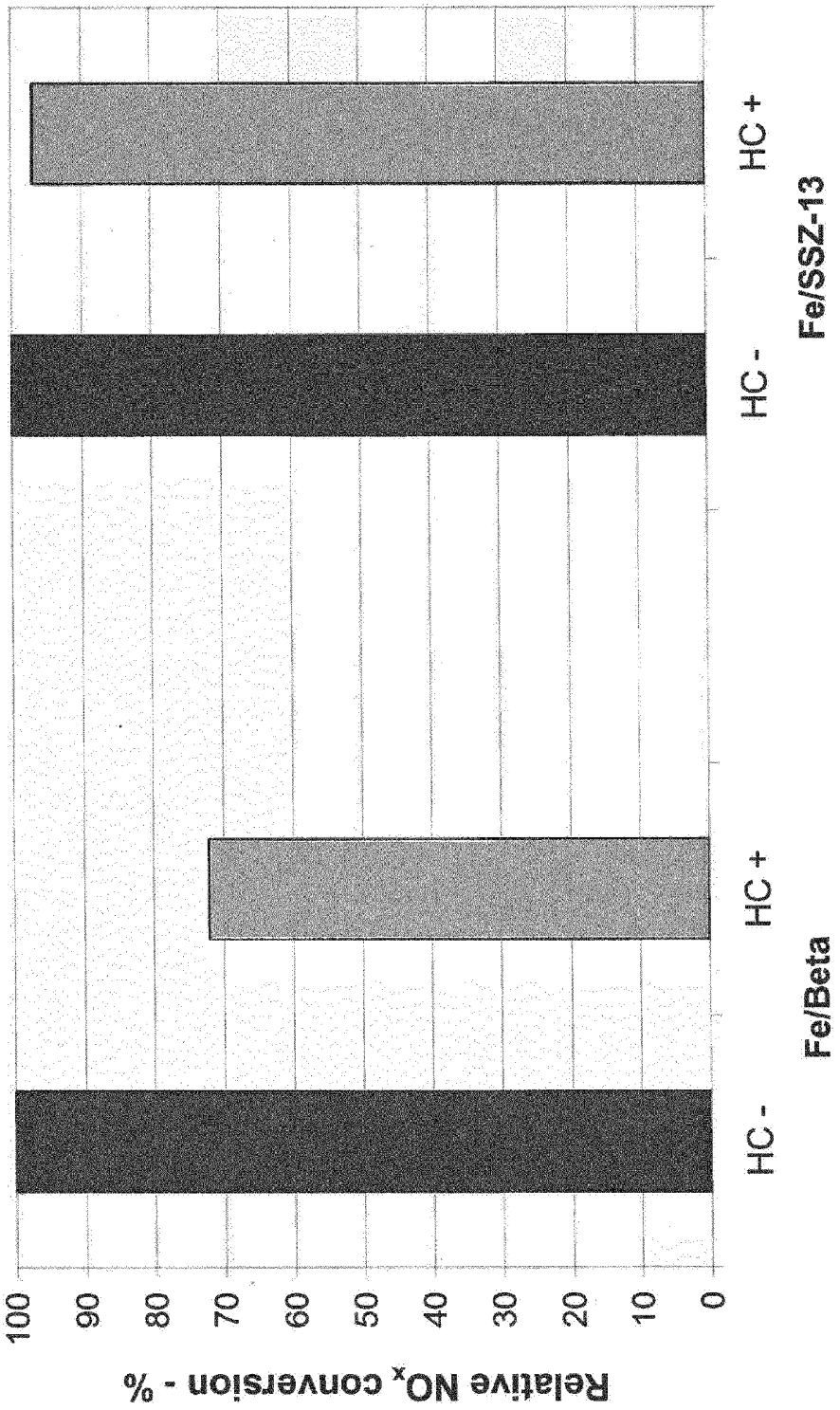

NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
Cu/Beta
Cu/SAPO-34
Fe/SAPO-34
Fe/SSZ-13
350C
Cu/Beta
Cu/SAPO-34
Fe/SAPO-34
Fe/SSZ-13
450C

Figure 20


Relative NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
HC -
HC +
Fe/Beta
HC -
HC +
Fe/SSZ-13

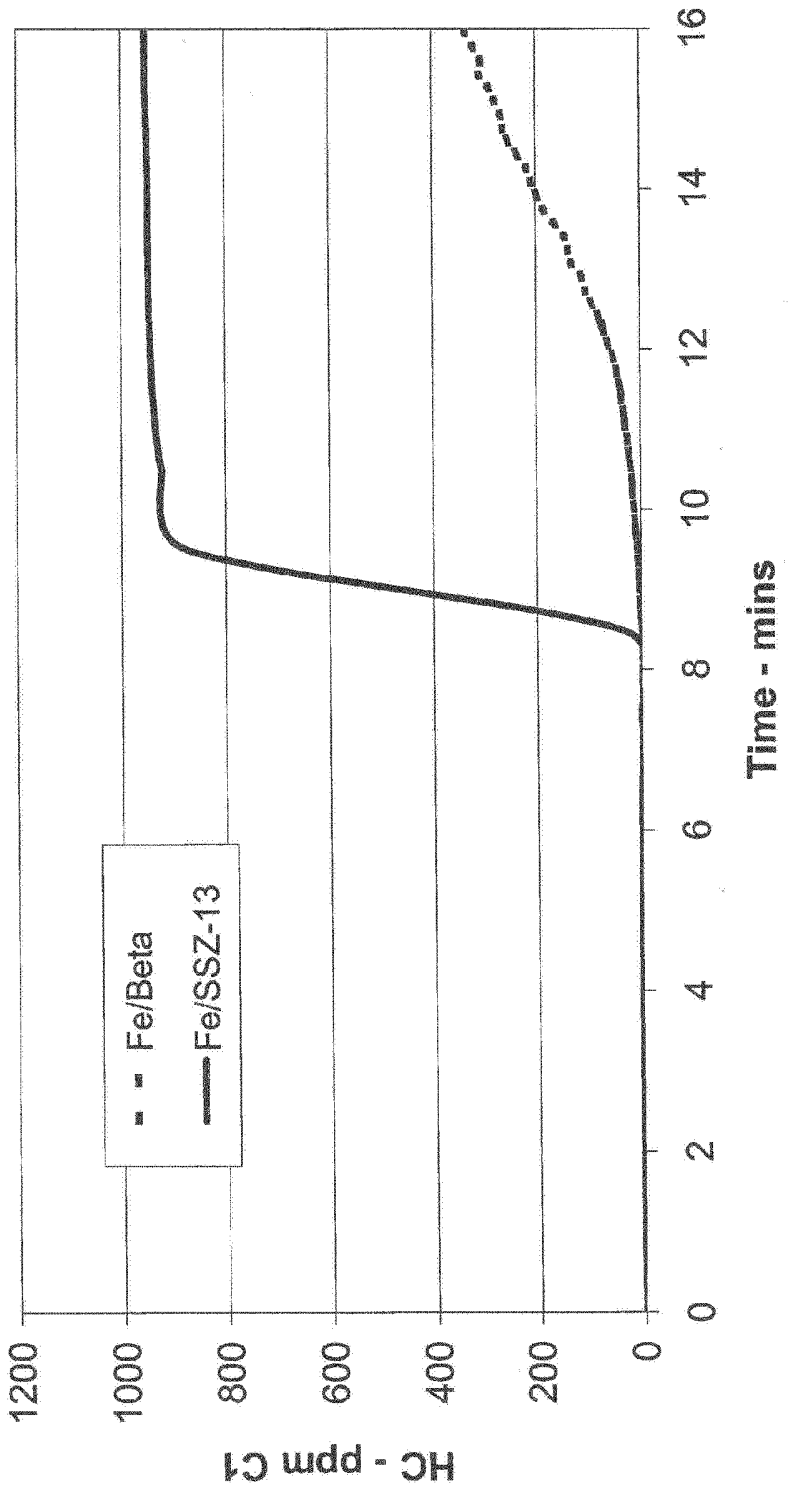

HC - ppm C1
1200
1000
800
600
400
200
0
0
2
4
6
8
10
12
14
16
Time - mins
Fe/Beta
Fe/SSZ-13

Figure 21

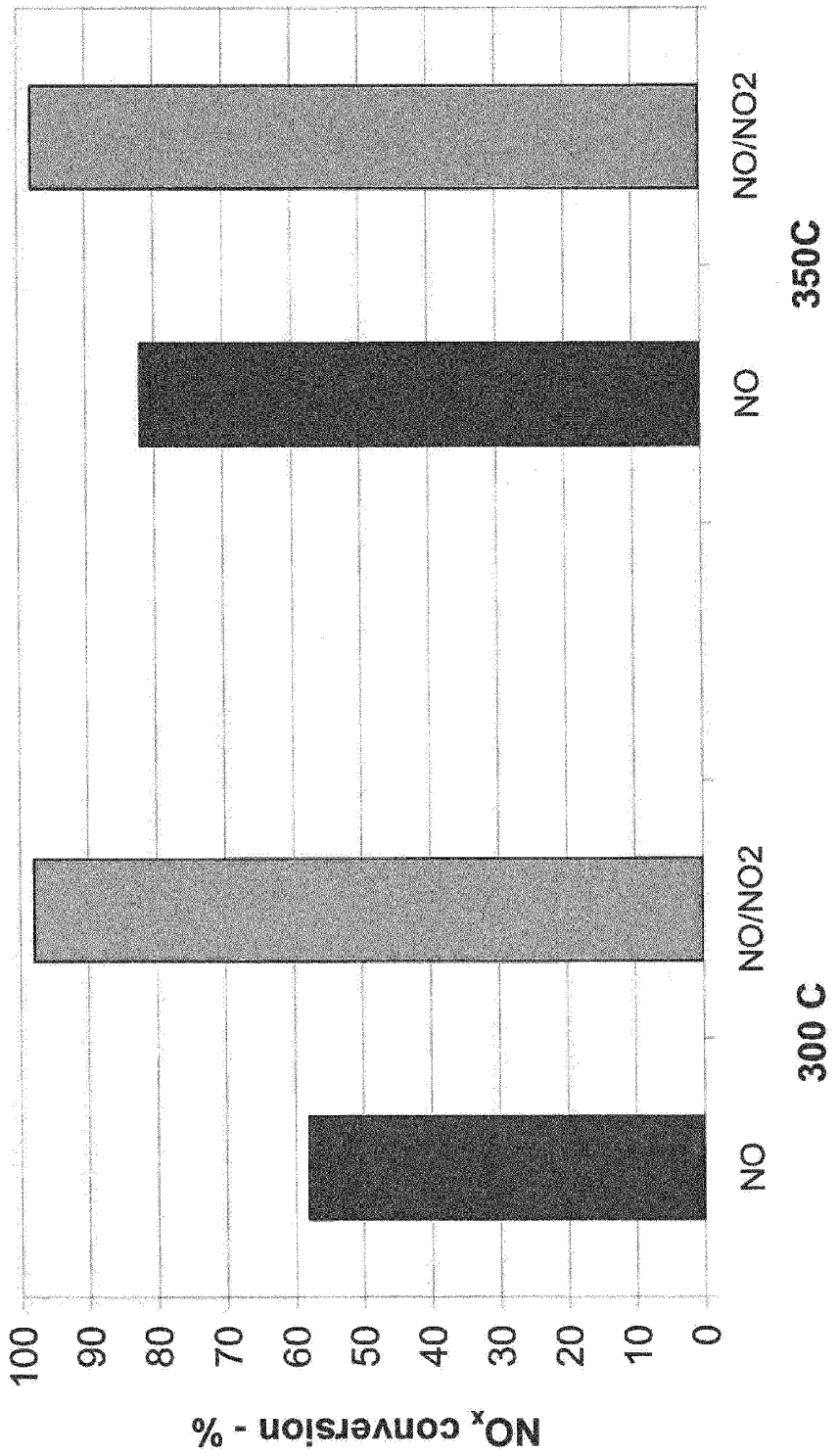

NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
NO
NO/NO2
300 C
NO
NO/NO2
350C

Figure 22

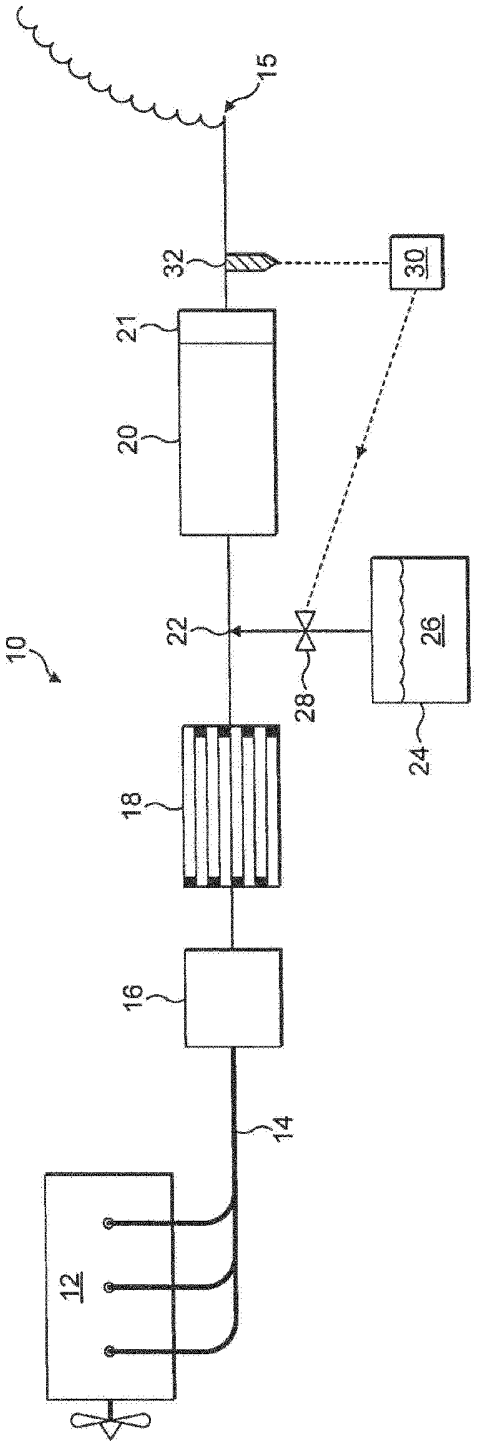


FIG. 23