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(54) **TRANSITION METAL/ZEOLITE SCR CATALYSTS**

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(57) **ABSTRACT**

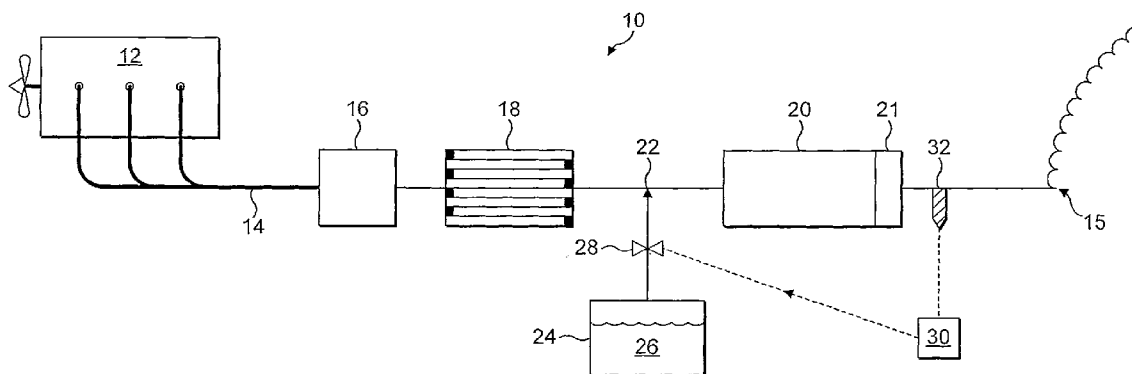
A method of converting nitrogen oxides in a gas to nitrogen by contacting the nitrogen oxides with a nitrogenous reducing agent in the presence of a zeolite catalyst containing at least one transition metal, wherein the zeolite is a small pore zeolite containing a maximum ring size of eight tetrahedral 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, Jr and Pt.

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(22) Filed: **Aug. 6, 2012**

**Related U.S. Application Data**

(63) Continuation of application No. 13/164,150, filed on Jun. 20, 2011, which is a continuation of application



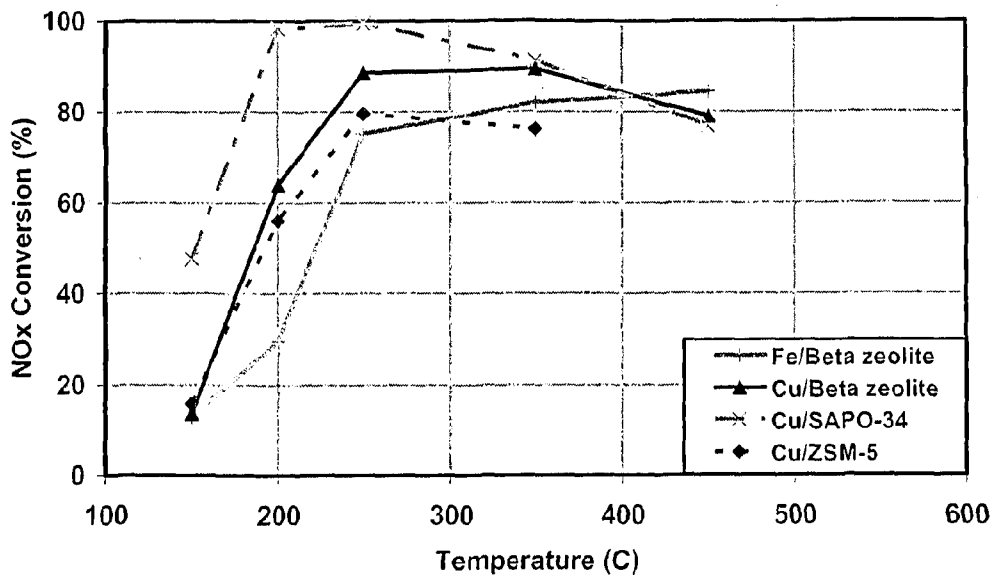


FIGURE 1

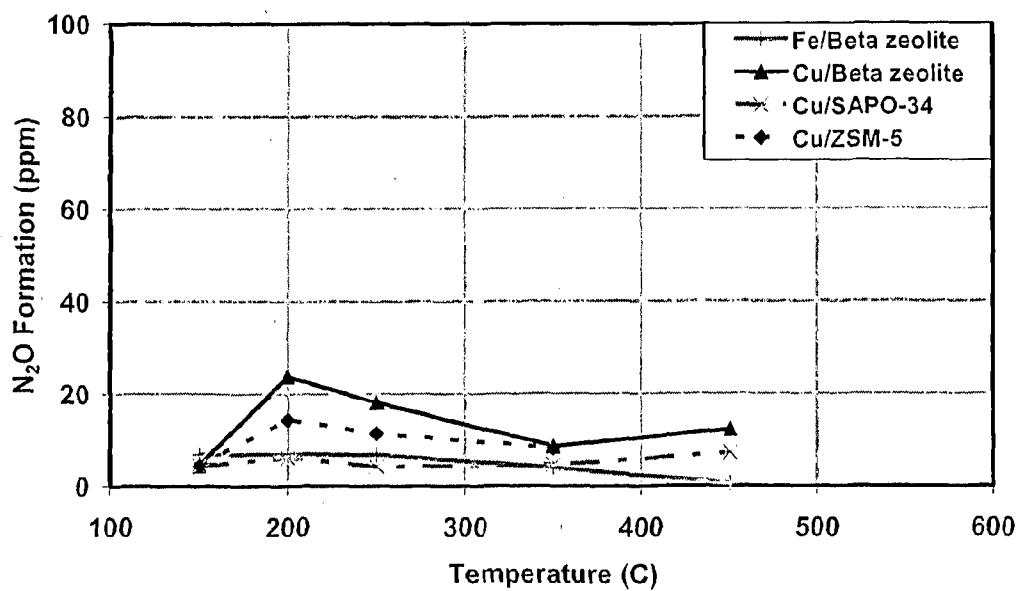


FIGURE 2

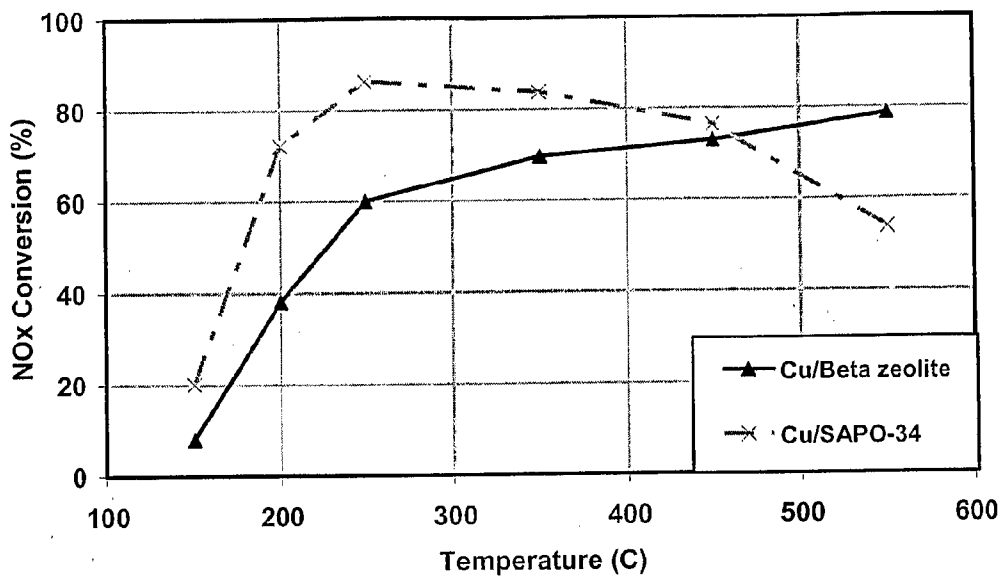


FIGURE 3

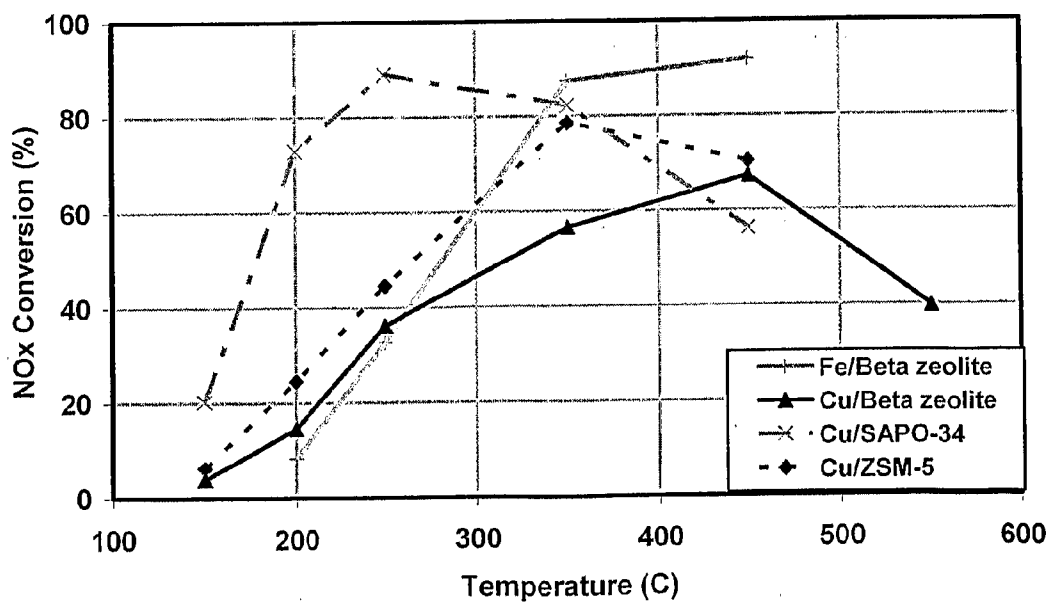


FIGURE 4

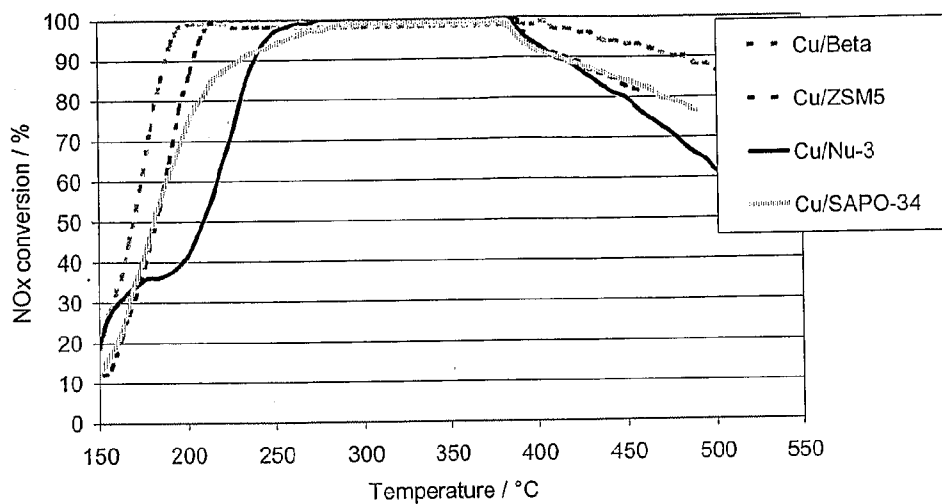


FIGURE 5

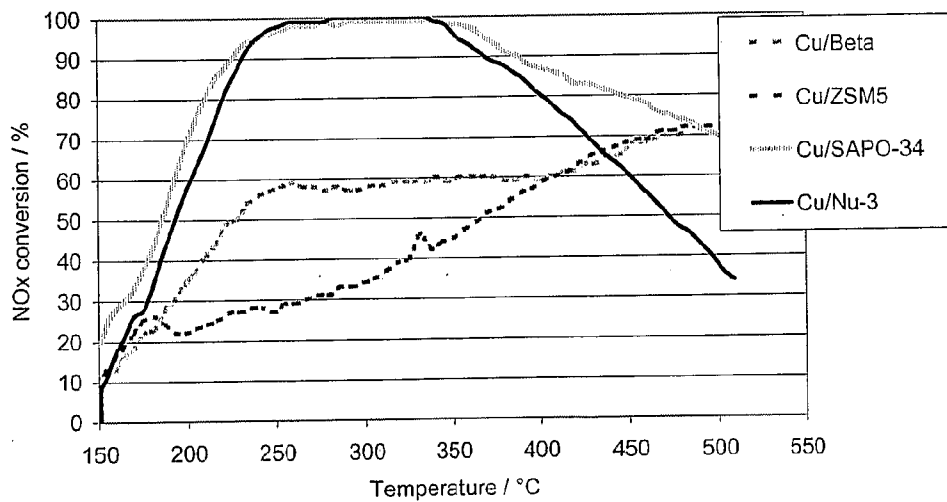


FIGURE 6

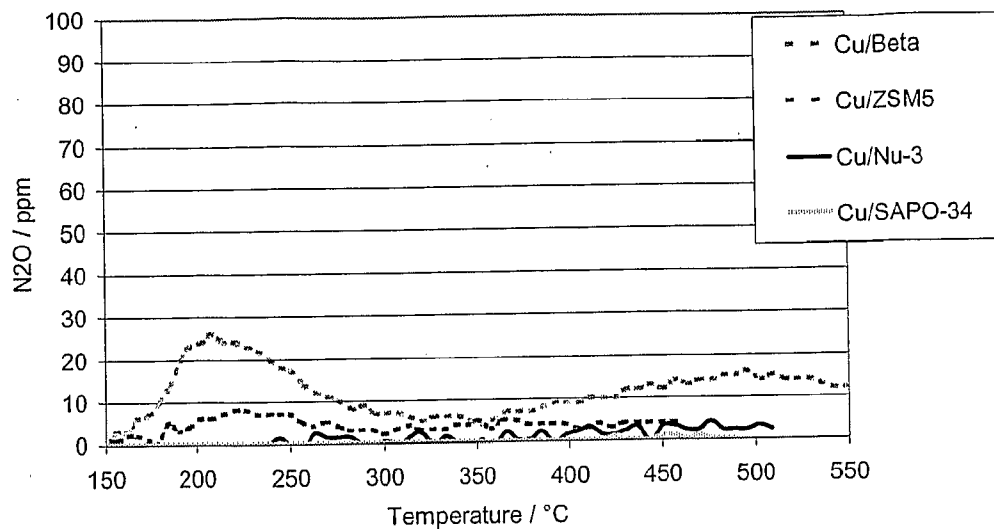


FIGURE 7

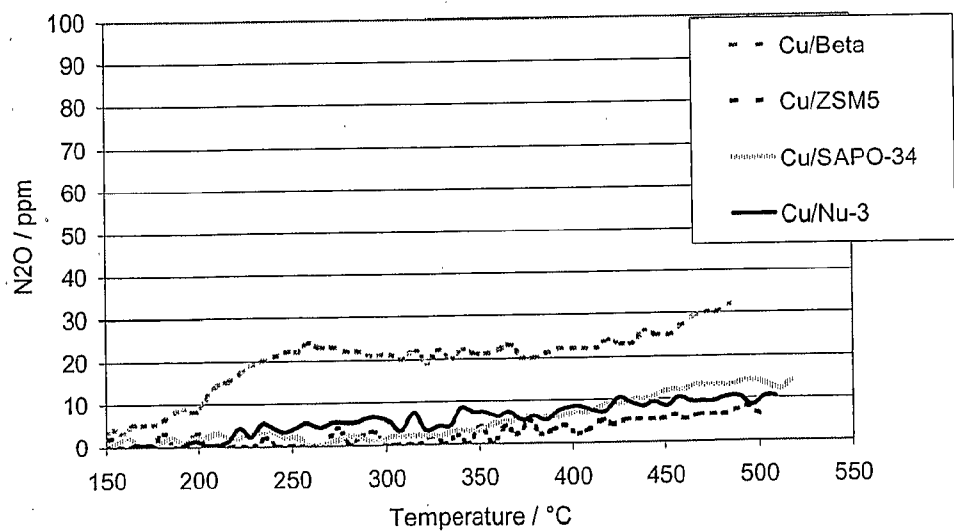


FIGURE 8

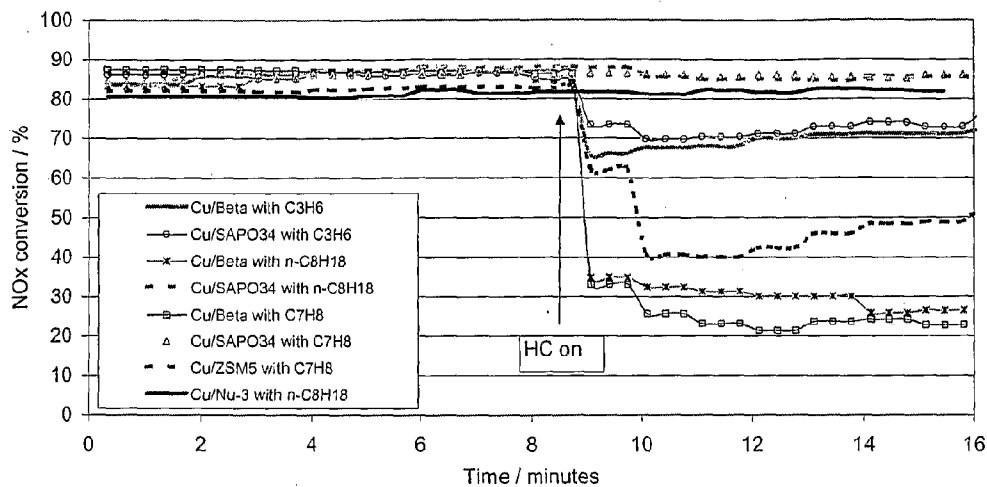


FIGURE 9

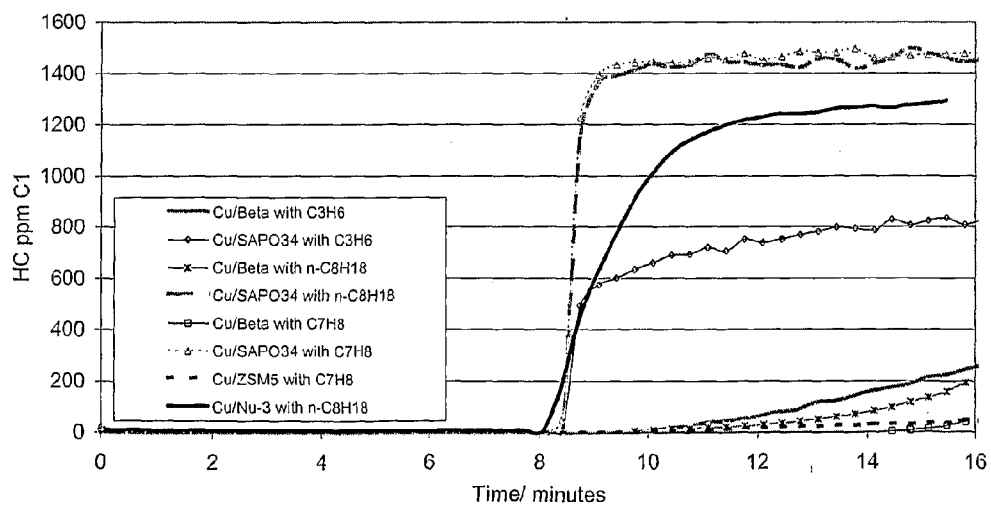


FIGURE 10

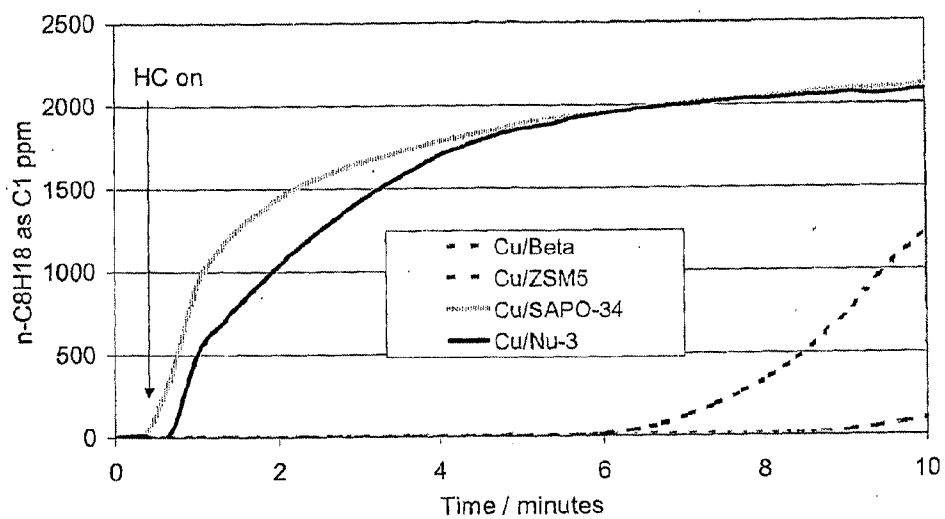


FIGURE 11

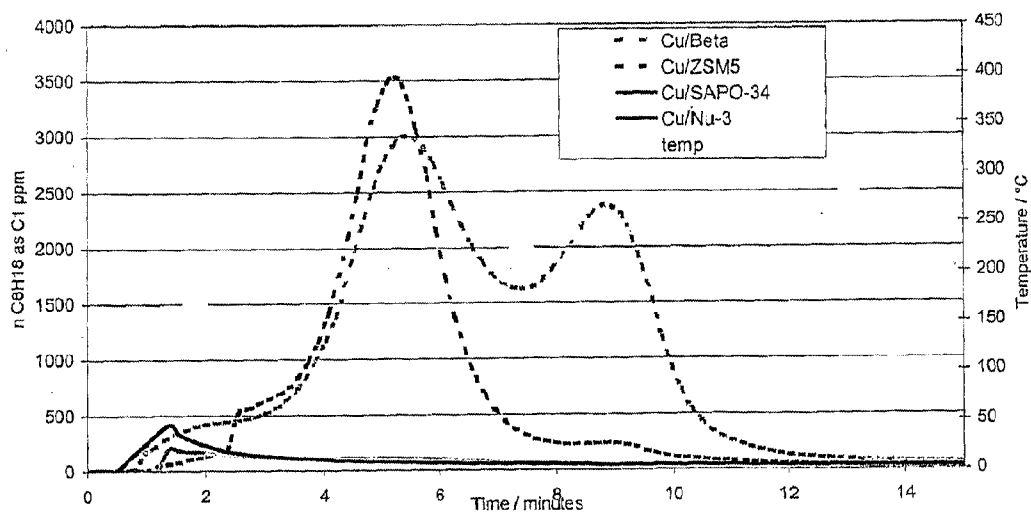


FIGURE 12

Figure 13

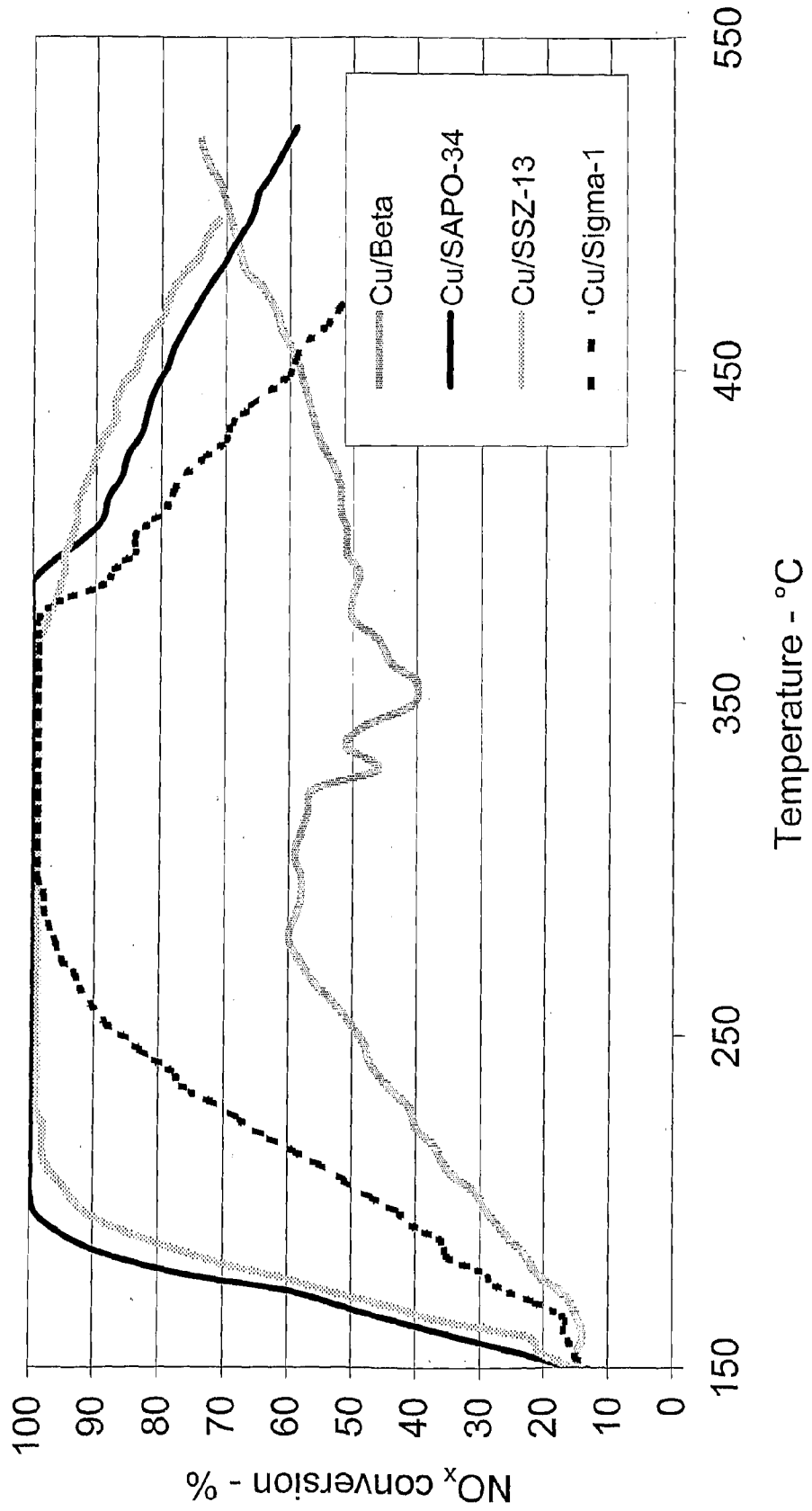




Figure 14

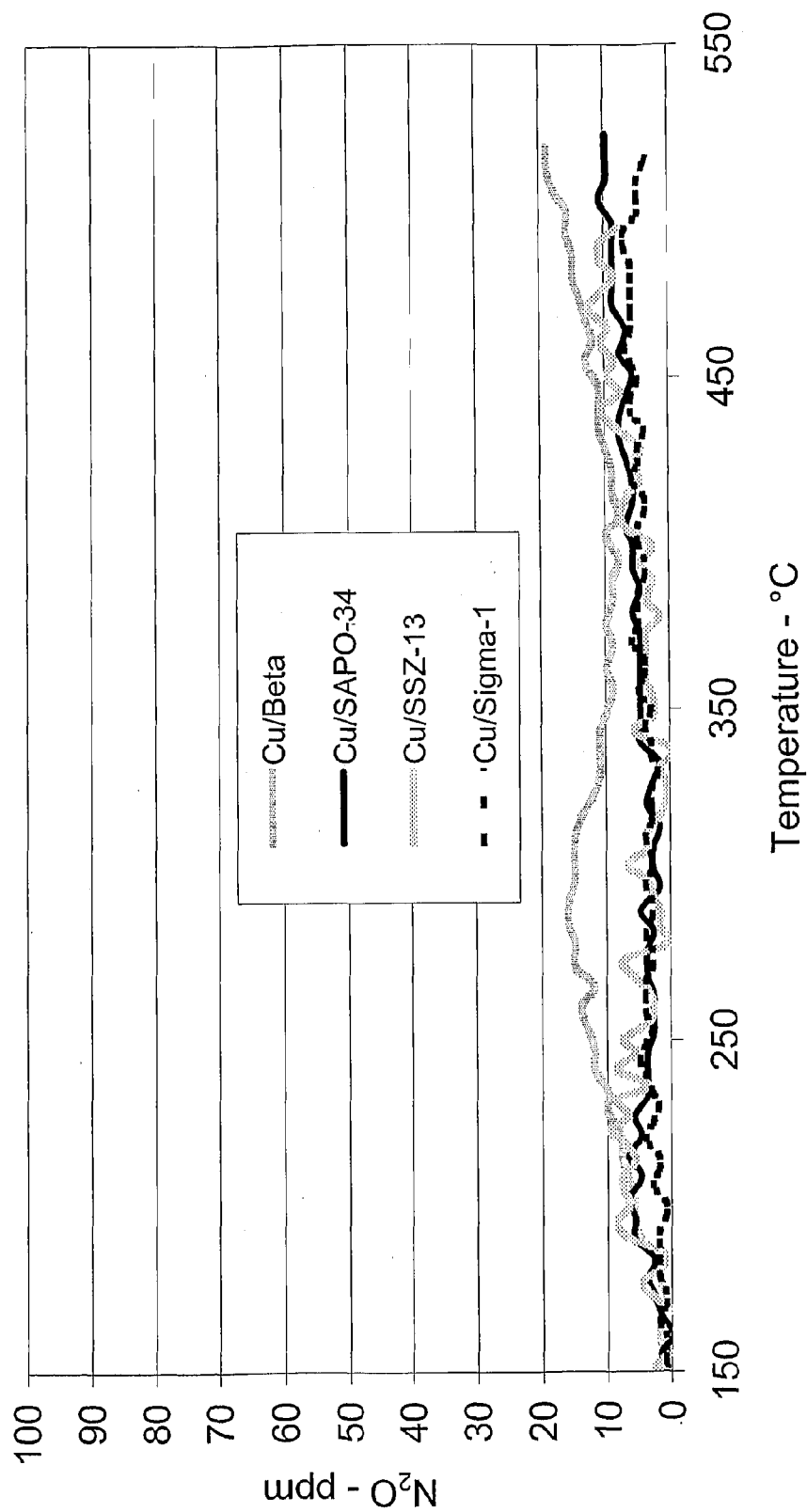


Figure 15

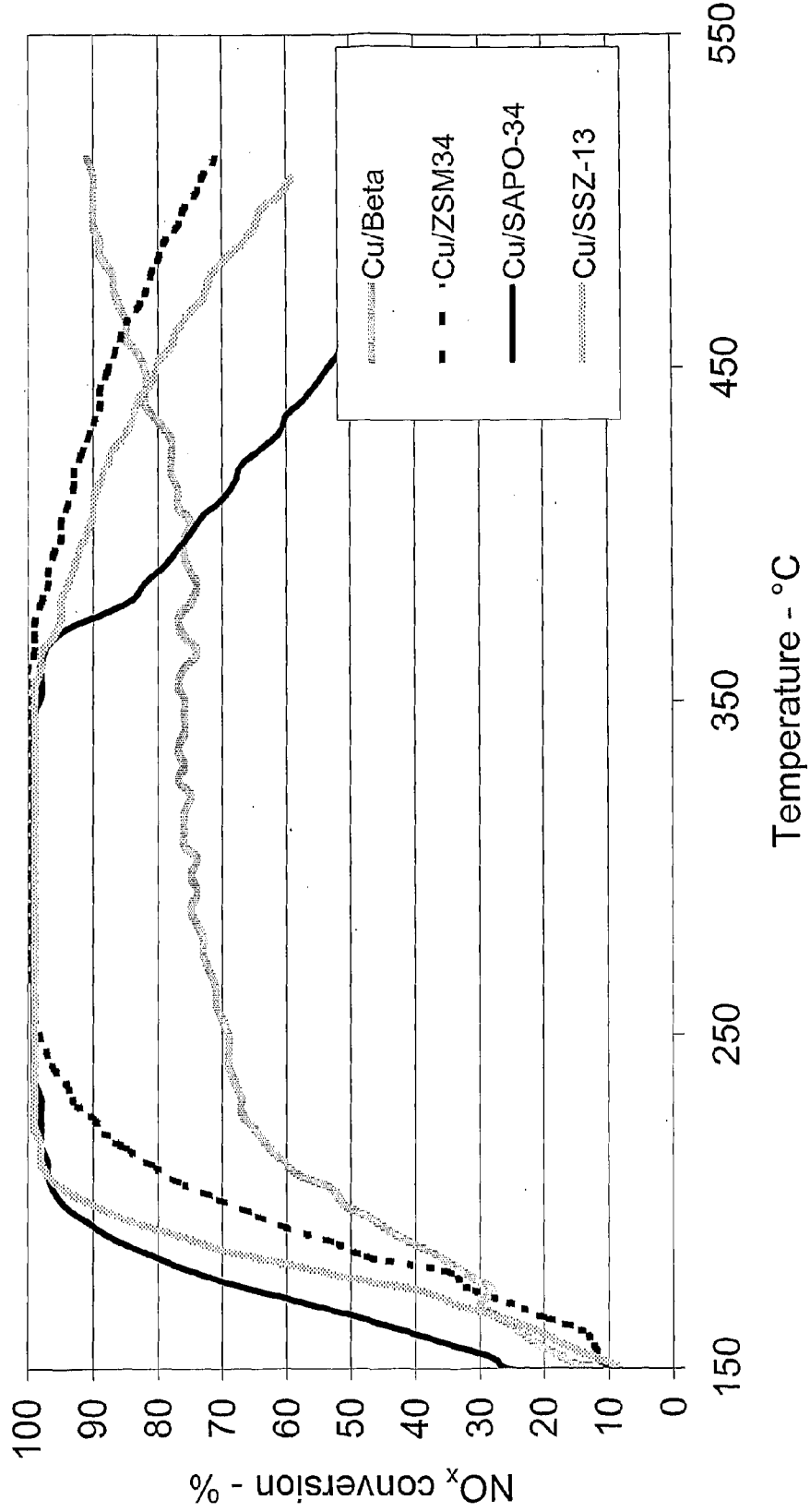


Figure 16

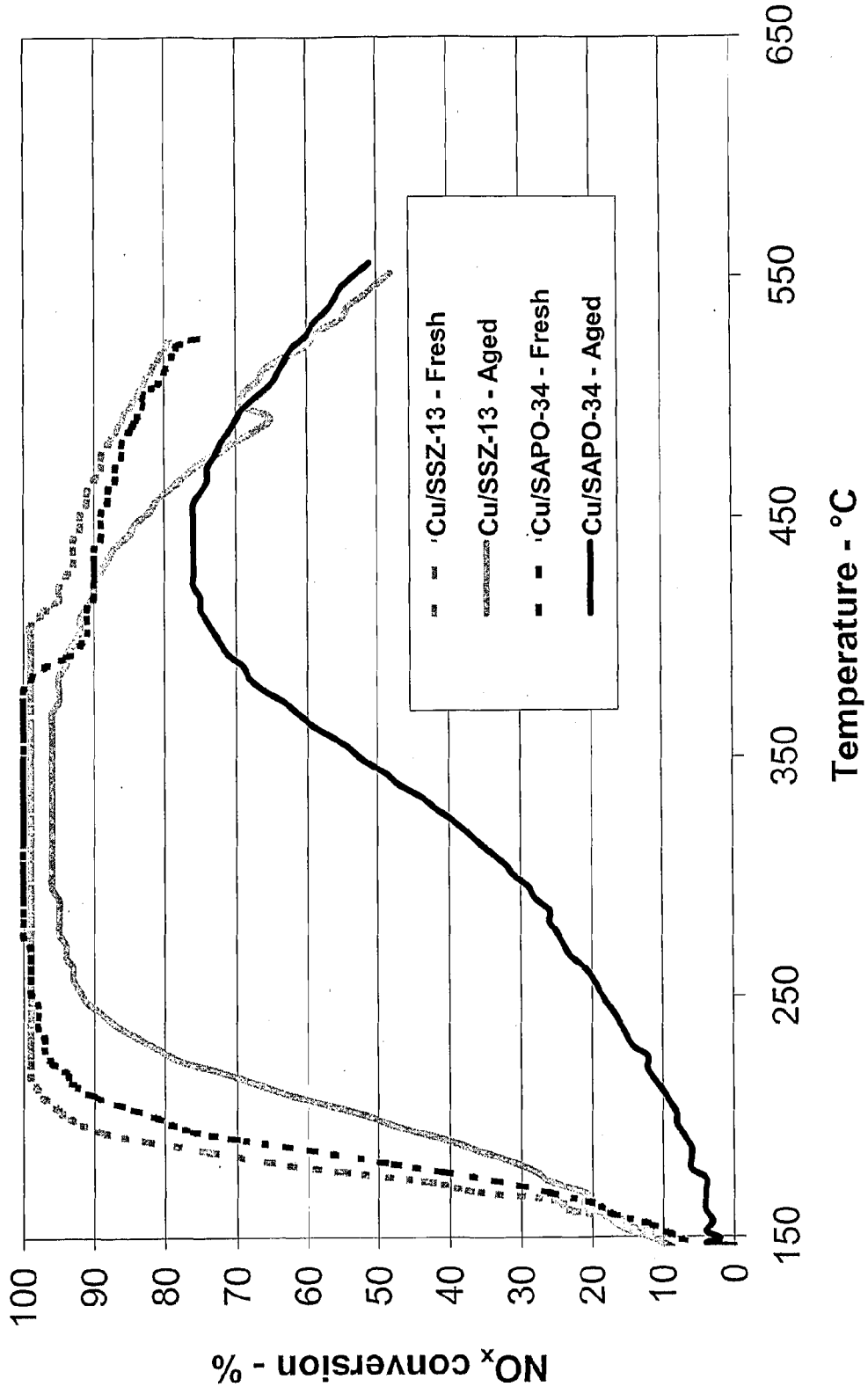


Figure 17

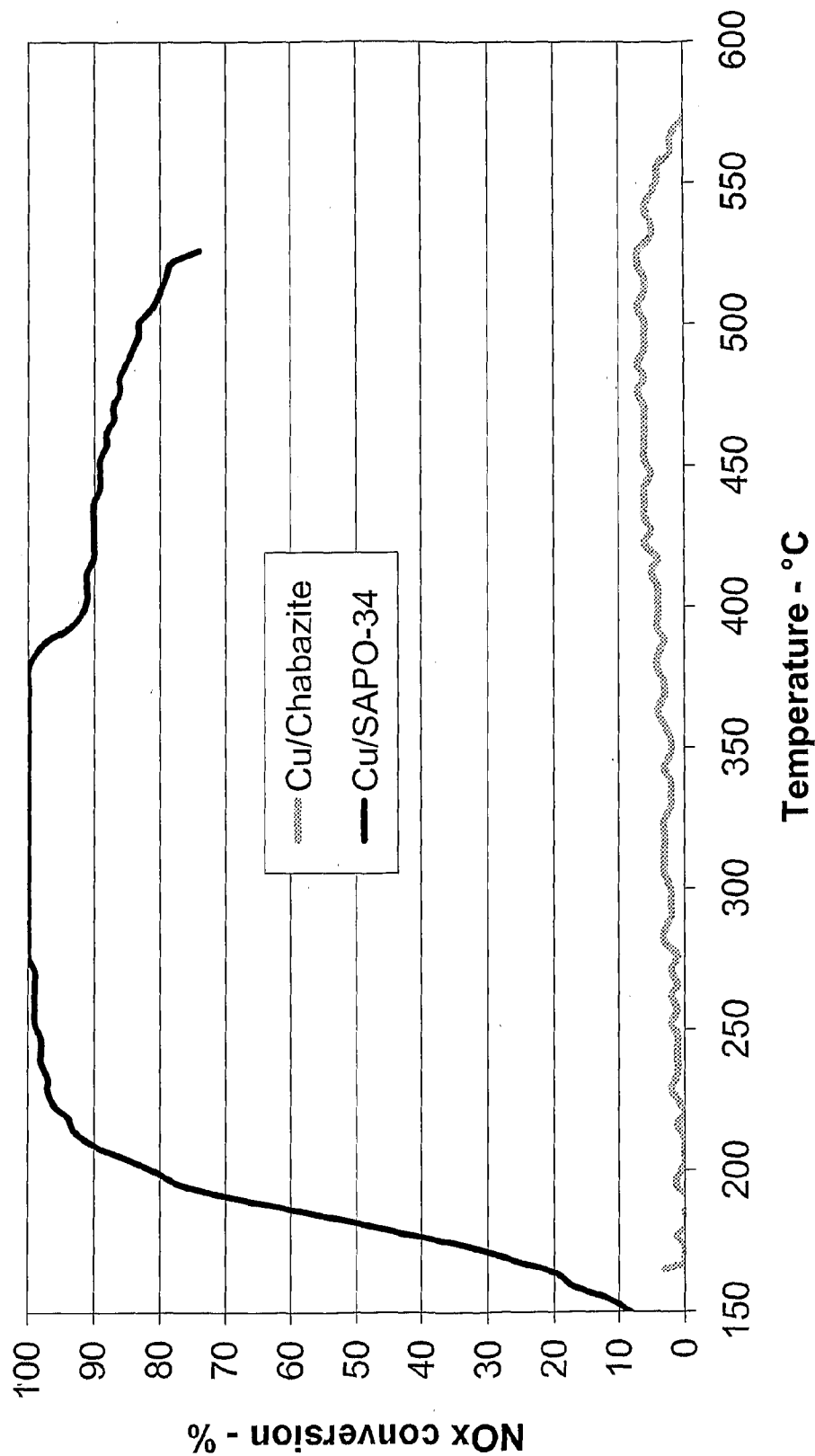


Figure 1B

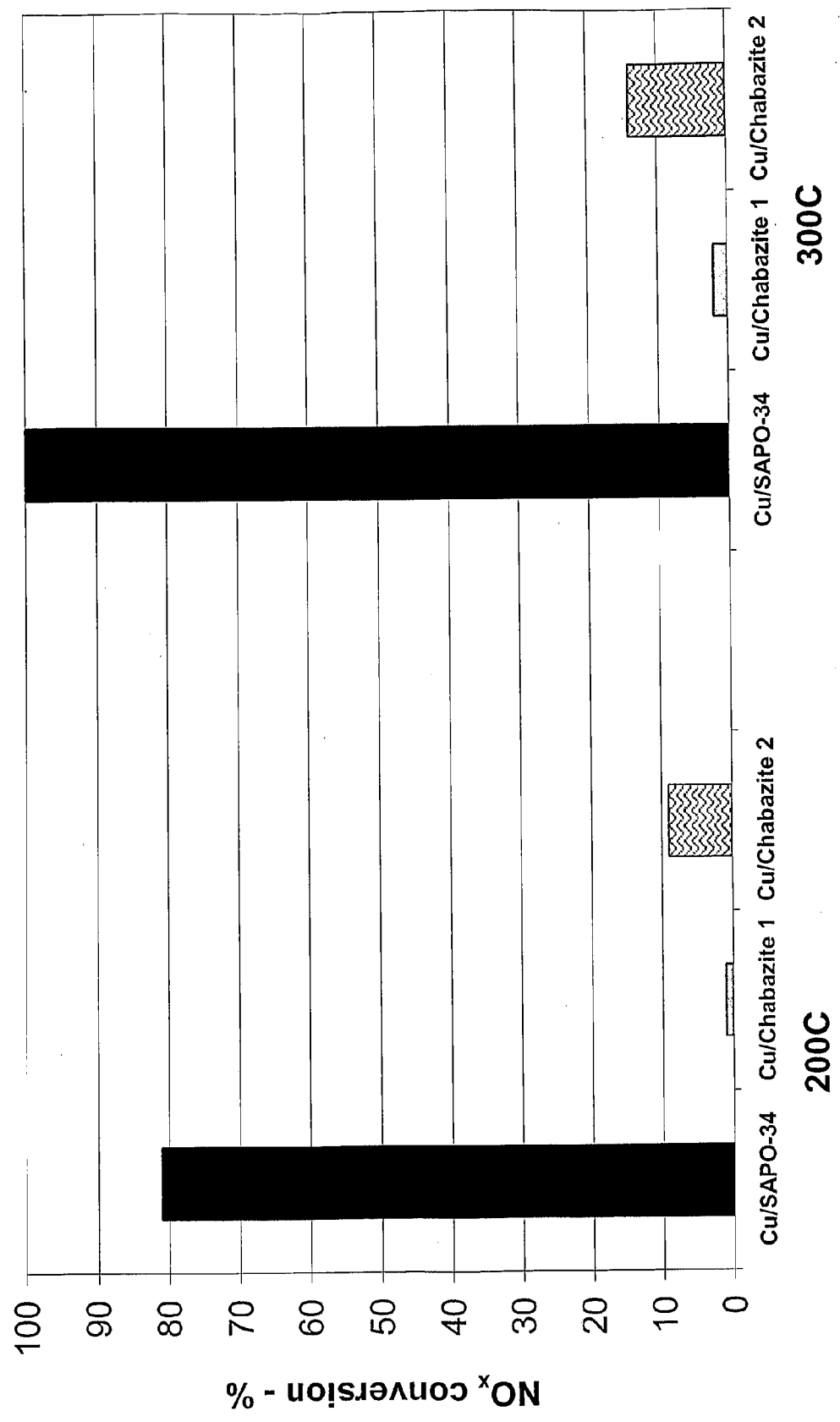


Figure 19

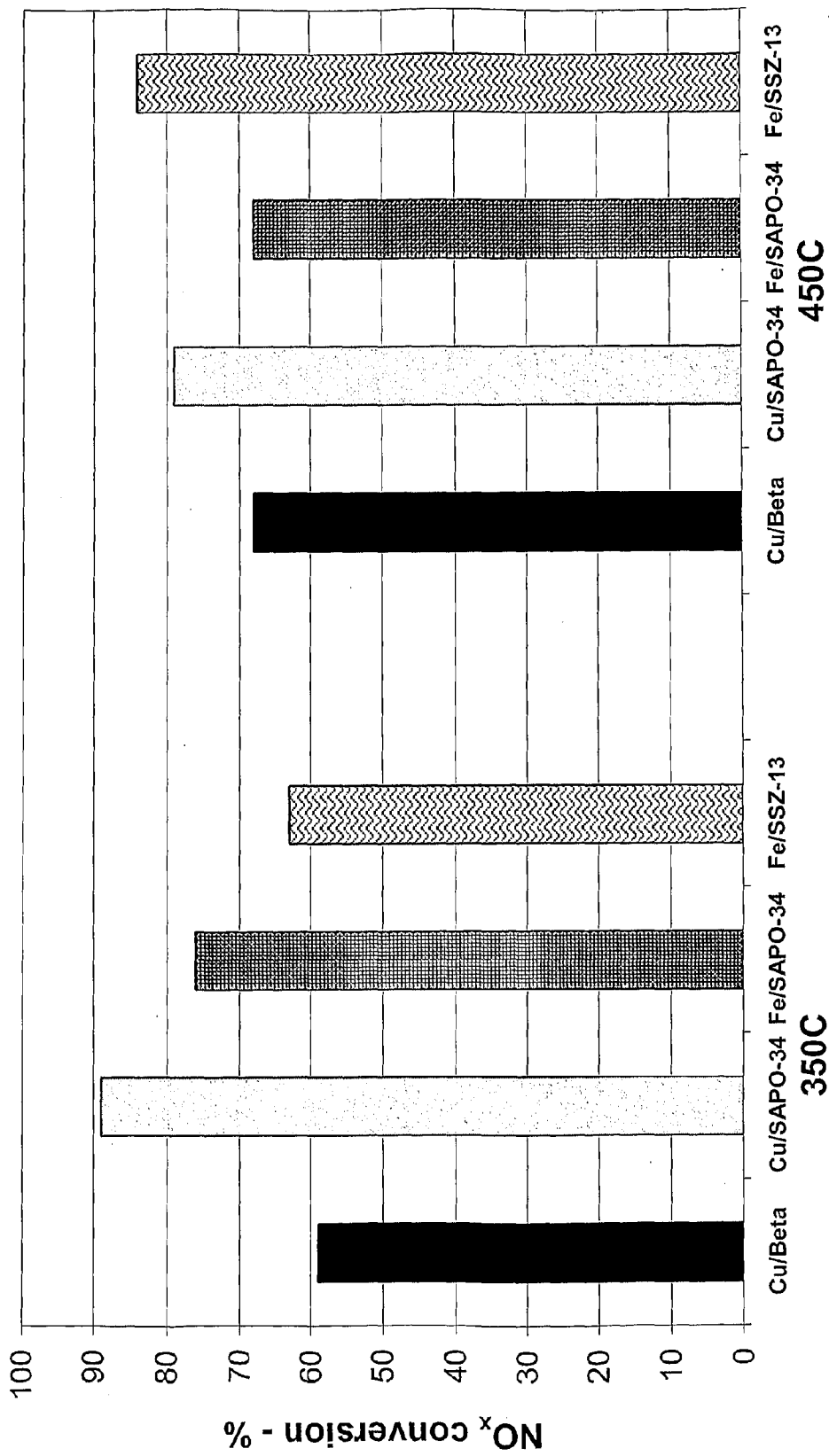


Figure 20

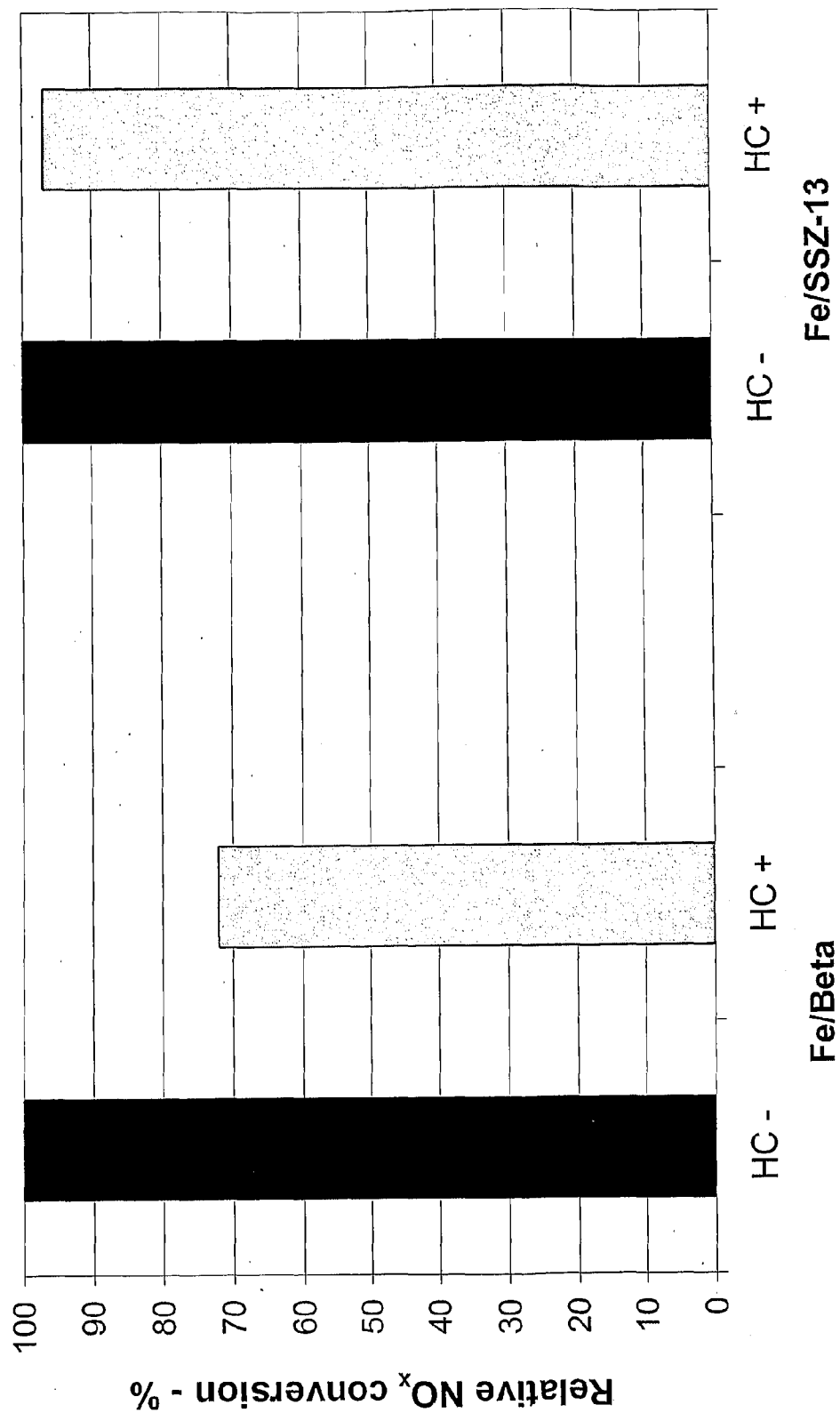


Figure 21

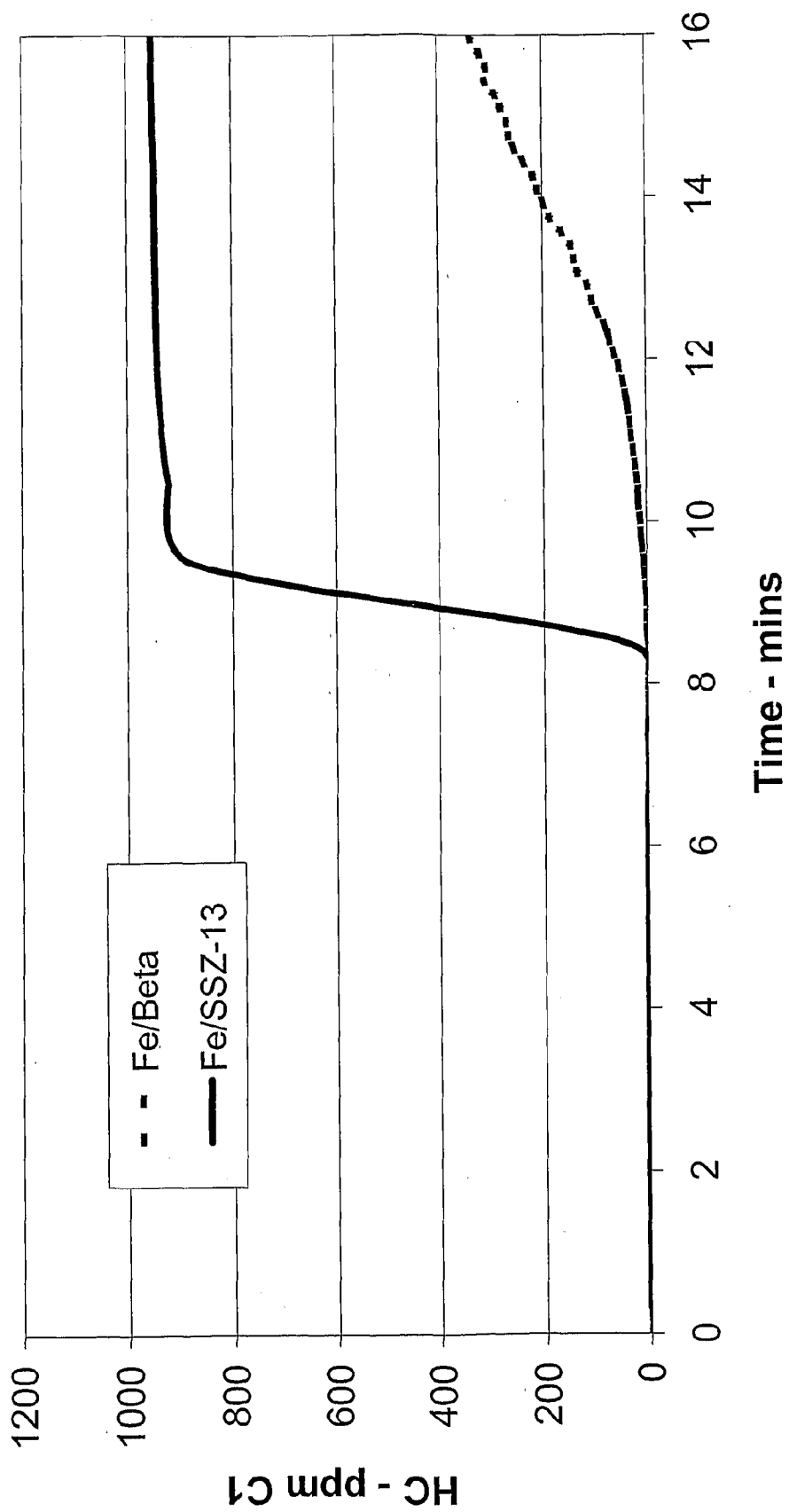
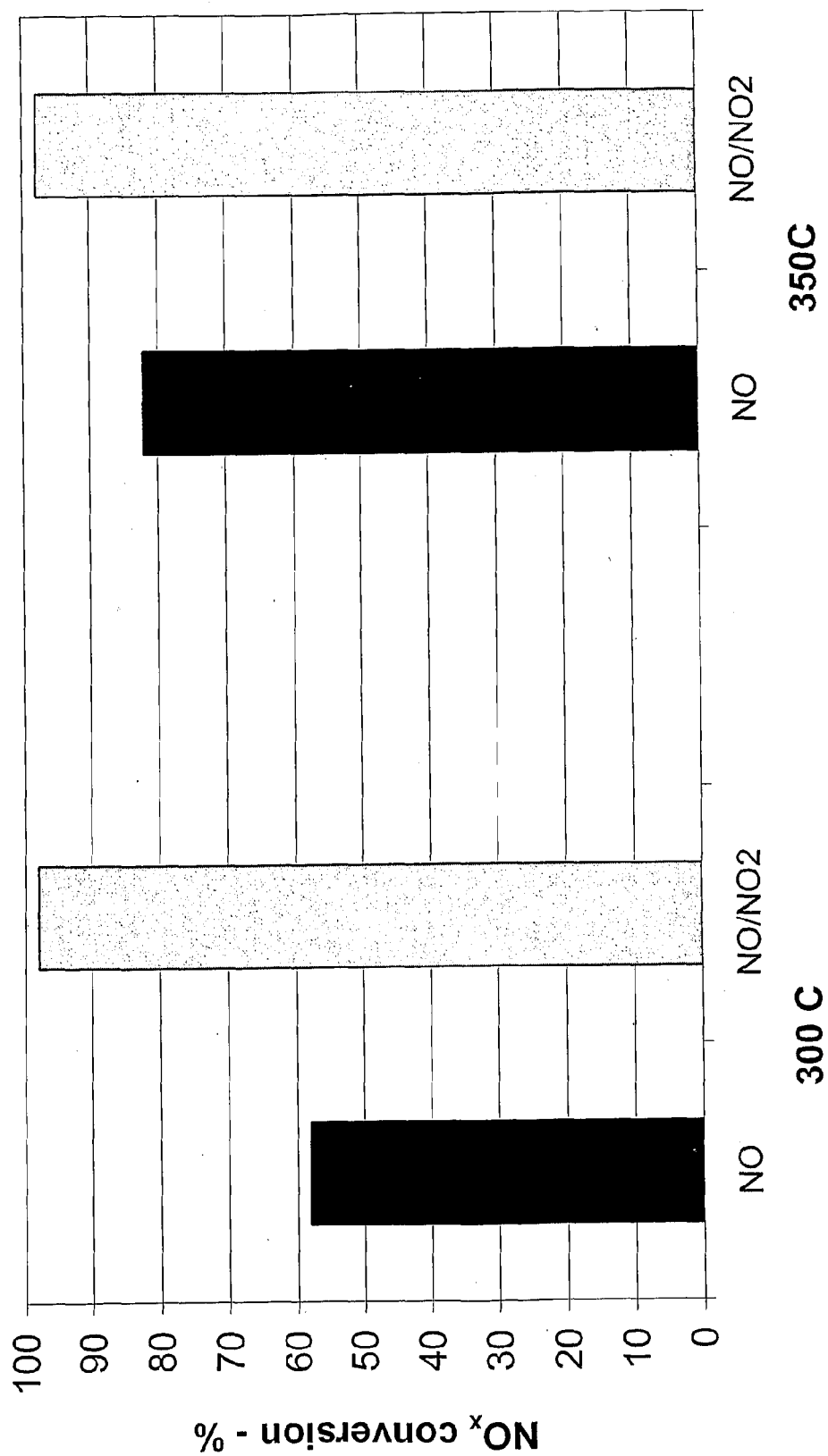




Figure 22



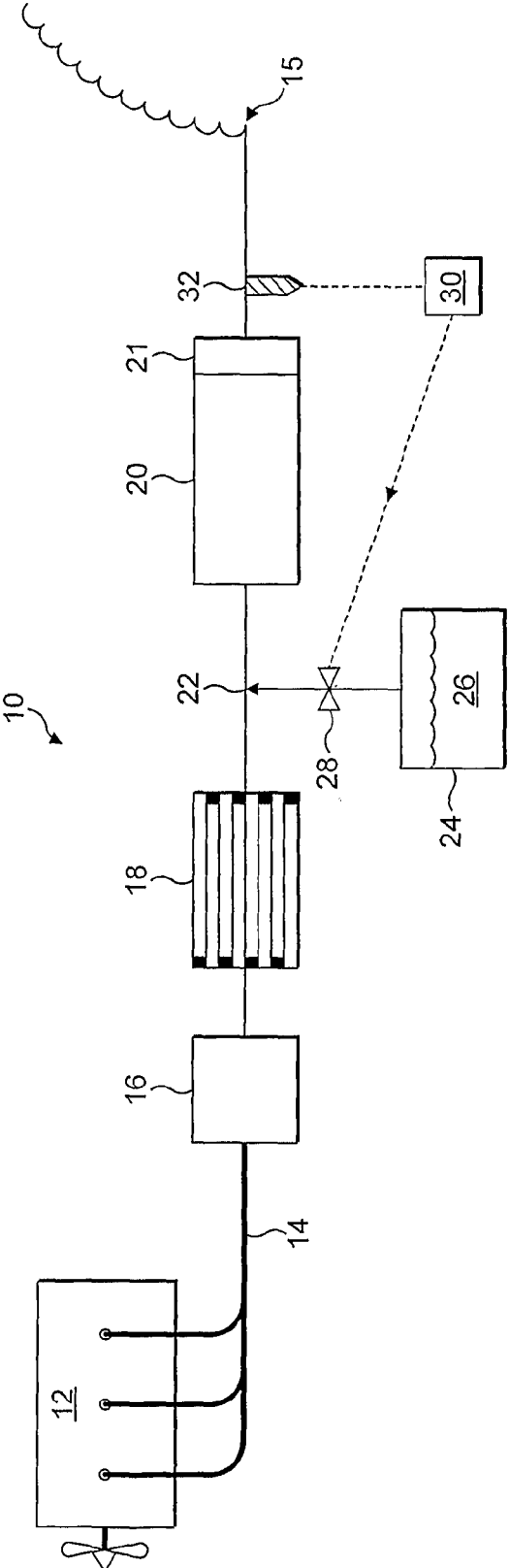


FIG. 23

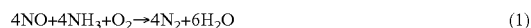
### TRANSITION METAL/ZEOLITE SCR CATALYSTS

**[0001]** This application is a continuation of U.S. application Ser. No. 13/164,150, filed on Jun. 20, 2011, which is a continuation of U.S. application Ser. No. 12/597,707, filed on May 7, 2010, which is a 371 of PCT/GB2008/001451, filed on Apr. 24, 2008, which in turn claims priority to PCT/GB2007/050216, filed on Apr. 26, 2007, the entire contents of which are fully incorporated herein by reference.

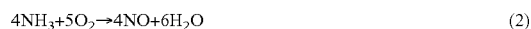
**[0002]** The present invention relates to a method of converting nitrogen oxides in a gas, such as an exhaust gas of a vehicular lean-burn internal combustion engine, to nitrogen by contacting the nitrogen oxides with a nitrogenous reducing agent in the presence of a transition metal-containing zeolite catalyst.

**[0003]** Selective catalytic reduction (SCR) of NO 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 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.

**[0004]** Several chemical reactions occur in an NH<sub>3</sub> SCR system, all of which represent desirable reactions that reduce NO to nitrogen. The dominant reaction is represented by reaction (1).



**[0005]** 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).



Also, side reactions may lead to undesirable products such as N<sub>2</sub>O, as represented by reaction (3).



**[0006]** Aluminosilicate zeolites are used as catalysts for SCR of NO with NH<sub>3</sub>. One application is to control NO 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 reduction activity than Fe-based zeolite catalysts.

**[0007]** 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.

**[0008]** In general, Cu-based zeolite catalysts are less thermally durable, and produce higher levels of N<sub>2</sub>O 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.

**[0009]** 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 with hydrocarbons (also known as lean NO 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 reducer (hydrocarbon or fuel) and a Cu-SAPO-34 NO 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 with NH<sub>3</sub> (or urea) reported in any literature to date.

**[0010]** WO 00/72965 discloses iron (Fe) exchanged zeolites for the selective catalytic reduction of nitrogen monoxide by ammonia for controlling NO 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.

**[0011]** U.S. Pat. No. 4,735,927 discloses an extruded-type NH<sub>3</sub>-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.

**[0012]** U.S. Pat. No. 5,417,949 also discloses an extruded-type NH<sub>3</sub>-SCR catalyst comprising a zeolite having a con-

straint 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)).

**[0013]** U.S. Pat. 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.

**[0014]** The disclosure of U.S. Pat. No. 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.

**[0015]** WO 2004/002611 discloses an NH<sub>3</sub>-SCR catalyst comprising a ceria-doped aluminosilicate zeolite.

**[0016]** U.S. Pat. No. 6,514,470 discloses a process for catalytically reducing NO 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.

**[0017]** Long et al. *Journal of Catalysis* 207 (2002) 274-285 reports on studies of Fe<sup>3+</sup>-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.

**[0018]** U.S. Pat. No. 4,961,917 discloses an NH<sub>3</sub>-SCR catalyst comprising a zeolite having a silica-to-alumina ratio of at least about 10, and a pore structure which is intercon-

nected 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<sub>3</sub> oxidation and reduced sulphur poisoning. Zeolite Beta and zeolite Y are two zeolites that meet the required definition.

**[0019]** U.S. Pat. No. 3,895,094 discloses an NH<sub>3</sub>-SCR process using zeolite catalysts of at least 6 Angstrom intercrystalline pore size. No mention is made of exchanging the zeolites with transition metals.

**[0020]** U.S. Pat. No. 4,220,632 also discloses an NH<sub>3</sub>-SCR process, this time using 3-10 Angstrom pore size zeolites of Na or H form.

**[0021]** WO 02/41991 discloses metal promoted zeolite Beta for NH<sub>3</sub>-SCR, wherein the zeolite is pre-treated so as to provide it with improved hydrothermal stability.

**[0022]** 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<sub>2</sub>—in particular low N<sub>2</sub>O 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.

**[0023]** According to one aspect, the invention provides 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.

**[0024]** 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.

**[0025]** 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 isotopic 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 isotopic 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 isotopic 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 isotopic 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](http://www.iza-online.org).

**[0026]** 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 arbi-

trary, 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 aluminosilicate isotypes such as SSZ-13, the naturally occurring chabazite has lower acidity than aluminosilicate 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).

**[0027]** The zeolite 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.

**[0028]** 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. Accordingly, we seek to exclude any specific small pore zeolites containing at least one transition metal that have been mentioned only in this context.

**[0029]** In this regard, in one embodiment, the zeolite catalyst is not one of Co, Ga, Mn, In or Zn or any combination of two or more thereof/epistilbite (see U.S. Pat. No. 6,514,470). In another embodiment, the transition metal-containing small pore zeolite is not Cu/chabazite, Mo/chabazite, Cu—Mo/chabazite, Cu/erionite, Mo/erionite or Cu—Mo/erionite (see U.S. Pat. No. 4,735,927). In a further embodiment, the transition metal-containing small pore zeolite is not Ce/erionite (see WO 2004/002611). In a further embodiment, the transition metal-containing small pore zeolite is not Fe/chabazite, Fe/ZK-5, Fe/ZK-4, Fe-rare-earth/chabazite, Fe-rare-earth/ZK-5 or Fe-rare-earth/ZK-4 (see WO 00/72965). Furthermore, although WO 00/72965 discloses the use of Ce/SAPO zeolites and Ce-rare-earth/SAPO zeolites in general, it does not disclose any particular small pore SAPO zeolites with application in the present invention, such as SAPO-17, SAPO-18, SAPO-34, SAPO-35, SAPO-39, SAPO-43 and SAPO-56. In yet a further embodiment, the transition metal-containing small pore zeolite is not Fe/chabazite, (see Long et al. *Journal of Catalysis* 207 (2002) 274-285). Whilst, for the reasons given hereinabove, we do not believe that U.S. Pat. No. 5,589,147 discloses the use of small pore zeolites containing at least one transition metal according to the method of the present invention, for safety, according to another embodiment, the zeolite catalyst is not any one of copper, zinc, chromium, manganese, cobalt, iron, nickel, rhodium, palladium, platinum, molybdenum, cerium or mixtures thereof/any one of aluminosilicate chabazite, aluminosilicate erionite, aluminosilicate ZSM-34 and SAPO-34. In another embodiment, the transition metal-containing zeolite catalyst is not LTA or Fe/CHA.

**[0030]** 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  $\text{NH}_4\text{Cl}$  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.

**[0031]** 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  $\text{FeCl}_2$  solution for ion exchange. Since the zeolite pores are relatively small, it is possible that a bulky coordination compound may not be able to gain access to the active sites located in the pores.

**[0032]** 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.

**[0033]** 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.

**[0034]** Aluminophosphate zeolites with application in the present invention include aluminophosphate (AIPO) zeolites, metal substituted zeolites (MeAIPO) zeolites, silico-aluminophosphate (SAPO) zeolites and metal substituted silico-aluminophosphate (MeAPSO) zeolites.

**[0035]** It will be appreciated that the invention extends to catalyst coatings and extruded-type substrate monoliths comprising both transition metal-containing small pore zeolites according to the invention and non-small pore zeolites (whether metallised or not) such as medium-, large- and meso-pore zeolites (whether containing transition metal(s) or not) because such a combination also obtains the advantages of using small pore zeolites per se. It should also be understood that the catalyst coatings and extruded-type substrate monoliths for use in the invention can comprise combinations of two or more transition metal-containing small pore zeolites. Furthermore, each small pore zeolite in such a combination can contain one or more transition metals, each being selected from the group defined hereinabove, e.g. a first small pore zeolite can contain both Cu and Fe and a second small pore zeolite in combination with the first small pore zeolite can contain Ce.

**[0036]** In this invention, we have discovered that transition metal-containing small pore zeolites are advantageous catalysts for SCR of NO with  $\text{NH}_3$ . Compared to transition metal-containing medium, large or meso-pore zeolite catalysts, transition metal-containing small pore zeolite catalysts demonstrate significantly improved NO reduction activity, especially at low temperatures. They also exhibit high selectivity to  $\text{N}_2$  (e.g. low  $\text{N}_2\text{O}$  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-17, SAPO-18, SAPO-34, SAPO-35, SAPO-39, SAPO-43 and SAPO-56.

**[0037]** In one embodiment, the small pore zeolite 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, UEL, UFI, VNI, YUG and ZON.

**[0038]** 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: (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  $\text{SiCl}_4$  (replaces Al in the zeolite 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. Pat. No. 5,958,818).

**[0039]** 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  $\text{NH}_3$  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 (3.16 Å) and  $\text{NH}_3$  (2.6 Å) is smaller than those of the typical hydrocarbons ( $\text{C}_3\text{H}_6$ ~4.5 Å, n- $\text{C}_8\text{H}_{18}$ ~4.30 Å and  $\text{C}_7\text{H}_8$ ~6.0 Å) 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 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 × 2.8, 3.5 × 3.5	Ring sizes - 8, 4
AEI	*AIPO-18 [Co—Al—P—O]-AEI SAPO-18 SIZ-8 SSZ-39	3D	3.8 × 3.8	Ring sizes - 8, 6, 4
AEN	*AIPO-EN3  AIPO-53(A) AIPO-53(B) [Ga—P—O]-AEN CFSAPO-1A CoIST-2 IST-2 JDF-2 MCS-1 MnAPO-14 Mu-10 UjO-12-500 UjO-12-as	2D	4.3 × 3.1, 2.7 × 5.0	Ring sizes - 8, 6, 4
AFN	*AIPO-14  [( $\text{C}_3\text{N}_2\text{H}_{12}$ )—[Mn—Al—P—O]- AFN GaPO-14	3D	1.9 × 4.6, 2.1 × 4.9, 3.3 × 4.0	Ring sizes - 8, 6, 4
AFT	*AIPO-52	3D	3.8 × 3.2, 3.8 × 3.6	Ring sizes - 8, 6, 4
AFX	*SAPO-56 MAPSO-56, M = Co, Mn, Zr SSZ-16	3D	3.4 × 3.6	Ring sizes - 8, 6, 4
ANA	*Analcime AlPO <sub>4</sub> -pollucite AIPO-24 Ammonioleucite [Al—Co—P—O]-ANA [Al—Si—P—O]-ANA [Cs—[Al—Ge—O]-ANA [Cs—[Be—Si—O]-ANA [Cs <sub>16</sub> [Cu <sub>8</sub> Si <sub>40</sub> O <sub>96</sub> ]- ANA [Cs—Fe][Si—O]-ANA [Cs—Na—(H <sub>2</sub> O)][Ga—Si—O]- ANA [Ga—Ge—O]-ANA	3D	4.2 × 1.6	Ring sizes - 8, 6, 4

TABLE 1-continued

Details of small pore zeolites with application in the present invention				
Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic structures	Dimensionality	Pore size (Å)	Additional info
	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 <sub>4</sub> )— [Be—B—P—O]-ANA  (NH <sub>4</sub> )— [Zn—Ga—P—O]-ANA [Zn—As—O]-ANA Ca-D Hsianghualite Leucite Na—B Pollucite Wairakite			
APC	*AIPO-C	2D	3.7 × 3.4, 4.7 × 2.0	Ring sizes - 8, 6, 4
	AIPO-H3 CoAPO-H3			
APD	*AIPO-D	2D	6.0 × 2.3, 5.8 × 1.3	Ring sizes - 8, 6, 4
	APO-CJ3			
ATT	*AIPO-12-TAMU	2D	4.6 × 4.2, 3.8 × 3.8	Ring sizes - 8, 6, 4
	AIPO-33 RMA-3			
CDO	*CDS-1	2D	4.7 × 3.1, 4.2 × 2.5	Ring sizes - 8, 5
	MCM-65 UZM-25			
CHA	*Chabazite AIPO-34	3D	3.8 × 3.8	Ring sizes - 8, 6, 4
	[Al—As—O]-CHA [Al—Co—P—O]-CHA  Co  [Be—P—O]-CHA  Co <sub>3</sub> (C <sub>6</sub> N <sub>4</sub> H <sub>24</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>9</sub>   [Be <sub>18</sub> P <sub>18</sub> O <sub>72</sub> ]-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) <sub>2</sub> )-UT-6 Phi SAPO-34 SAPO-47 SSZ-13 UjO-21 Willhendersonite ZK-14 ZYT-6			

TABLE 1-continued

Details of small pore zeolites with application in the present invention				
Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic structures	Dimensionality	Pore size (Å)	Additional info
DDR	*Deca-dodecasil 3R [B—Si—O]-DDR	2D	4.4 × 3.6	Ring sizes - 8, 6, 5, 4
DFT	Sigma-1 ZSM-58 *DAF-2 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	3D	4.1 × 4.1, 4.7 × 1.8	Ring sizes - 8, 6, 4
EAB	*TMA-E Bellbergite	2D	5.1 × 3.7	Ring sizes - 8, 6, 4
EDI	*Edingtonite [(C <sub>3</sub> H <sub>12</sub> N <sub>2</sub> ) <sub>2.5</sub> ] [Zn <sub>3</sub> P <sub>3</sub> O <sub>20</sub> ]-EDI [Co—Al—P—O]-EDI [Co—Ga—P—O]-EDI [Li—[Al—Si—O]-EDI [Rb <sub>7</sub> Na(H <sub>2</sub> O) <sub>3</sub> ] [Ga <sub>8</sub> Si <sub>12</sub> O <sub>40</sub> ]-EDI [Zn—As—O]-EDI K—F Linde F Zeolite N	3D	2.8 × 3.8, 3.1 × 2.0	Ring sizes - 8, 4
EPI	*Epistilbite	2D	4.5 × 3.7, 3.6 × 3.6	Ring sizes - 8, 4
ERI	*Erionite AIPO-17 Linde T LZ-220 SAPO-17 ZSM-34	3D	3.6 × 5.1	Ring sizes - 8, 6, 4
GIS	*Gismondine Amicite [Al—Co—P—O]-GIS [Al—Ge—O]-GIS [Al—P—O]-GIS [Be—P—O]-GIS [(C <sub>3</sub> H <sub>12</sub> N <sub>2</sub> ) <sub>4</sub> ] [Be <sub>8</sub> P <sub>8</sub> O <sub>32</sub> ]-GIS [(C <sub>3</sub> H <sub>12</sub> N <sub>2</sub> ) <sub>4</sub> ] [Zn <sub>8</sub> P <sub>8</sub> O <sub>32</sub> ]-GIS [Co—Al—P—O]-GIS [Co—Ga—P—O]-GIS [Co—P—O]-GIS [Cs <sub>4</sub> ][Zn <sub>4</sub> B <sub>4</sub> P <sub>8</sub> O <sub>32</sub> ]-GIS [Ga—Si—O]-GIS [Mg—Al—P—O]-GIS [(NH <sub>4</sub> ) <sub>4</sub> ][Zn <sub>4</sub> B <sub>4</sub> P <sub>8</sub> O <sub>32</sub> ]-GIS [Rb <sub>4</sub> ][Zn <sub>4</sub> B <sub>4</sub> P <sub>8</sub> O <sub>32</sub> ]-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	3D	4.5 × 3.1, 4.8 × 2.8	Ring sizes - 8, 4



TABLE 1-continued

Details of small pore zeolites with application in the present invention				
Zeolite Framework Type (by Framework Type Code)	Type material* and illustrative isotypic structures	Dimensionality	Pore size (Å)	Additional info
GOO	Na-P1 Na-P2 SAPO-43 TMA-gismondine *Goosecreekite	3D	2.8 × 4.0, 2.7 × 4.1, 4.7 × 2.9	Ring sizes - 8, 6, 4
IHW	*ITQ-32	2D	3.5 × 4.3	Ring sizes - 8, 6, 5, 4
ITE	*ITQ-3	2D	4.3 × 3.8, 2.7 × 5.8	Ring sizes - 8, 6, 5, 4
ITW	Mu-14 SSZ-36 *ITQ-12	2D	5.4 × 2.4, 3.9 × 4.2	Ring sizes - 8, 6, 5, 4
LEV	*Levyne AIPO-35 CoDAF-4 LZ-132 NU-3 RUB-1 [B—Si—O]-LEV SAPO-35 ZK-20 ZnAPO-35	2D	3.6 × 4.8	Ring sizes - 8, 6, 4
KFI	ZK-5 [18-crown-6][Al—Si—O]-KFI KFI [Zn—Ga—As—O]-KFI (Cs,K)-ZK-5 P Q	3D	3.9 × 3.9	Ring sizes - 8, 6, 4
MER	*Merlinoite  [Al—Co—P—O]-MER [Ba—[Al—Si—O]-MER [Ba—Cl—[Al—Si—O]-MER K-M Linde W Zeolite W	3D	3.5 × 3.1, 3.6 × 2.7, 5.1 × 3.4, 3.3 × 3.3	Ring sizes - 8, 4
MON	*Montesommaite	2D	4.4 × 3.2, 3.6 × 3.6	Ring sizes - 8, 5, 4
NSI	[Al—Ge—O]-MON *Nu-6(2)	2D	2.6 × 4.5, 2.4 × 4.8	Ring sizes - 8, 6, 5
OWE	EU-20 *UiO-28	2D	4.0 × 3.5, 4.8 × 3.2	Ring sizes - 8, 6, 4
PAU	ACP-2 *Paulingite [Ga—Si—O]-PAU	3D	3.6 × 3.6	Ring sizes - 8, 6, 4
PHI	ECR-18 *Phillipsite	3D	3.8 × 3.8, 3.0 × 4.3, 3.3 × 3.2	Ring sizes - 8, 4
RHO	[Al—Co—P—O]-PHI DAF-8 Harmotome Wellsite ZK-19 *Rho [Be—As—O]-RHO [Be—P—O]-RHO [Co—Al—P—O]-RHO [H—[Al—Si—O]-RHO [Mg—Al—P—O]-RHO	3D	3.6 × 3.6	Ring sizes - 8, 6, 4

TABLE 1-continued

Details of small pore zeolites 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
RTH	[Mn—Al—P—O]-RHO  Na <sub>16</sub> CS <sub>8</sub>   [Al <sub>24</sub> Ge <sub>24</sub> O <sub>96</sub> ]-RHO  NH <sub>4</sub> — Al—Si—O]-RHO  Rb— Be—As—O]-RHO Gallosilicate ECR-10 LZ-214 Pahasapaite	2D	4.1 × 3.8, 5.6 × 2.5	Ring sizes - 8, 6, 5, 4
	*RUB-13			
SAT	SSZ-36	3D	5.5 × 3.0	Ring sizes - 8, 6, 4
	SSZ-50			
SAV	*STA-2	3D	3.8 × 3.8, 3.9 × 3.9	Ring sizes - 8, 6, 4
SBN	*Mg-STA-7	3D	3.8 × 3.8, 3.9 × 3.9	Ring sizes - 8, 6, 4
	Co-STA-7	3D	TBC	Ring sizes - 8, 4, 3
	Zn-STA-7			
SIV	*UCSB-9 SU-46	3D	3.5 × 3.9, 3.7 × 3.8, 3.8 × 3.9	Ring sizes - 8, 4
THO	*SIZ-7	3D	2.3 × 3.9, 4.0 × 2.2, 3.0 × 2.2	Ring sizes - 8, 4
TSC	*Thomsonite	3D	2.3 × 3.9, 4.0 × 2.2, 3.0 × 2.2	Ring sizes - 8, 4
	[Al—Co—P—O]-THO	3D	4.2 × 4.2, 5.6 × 3.1	Ring sizes - 8, 6, 4
	[Ga—Co—P—O]-THO			
	Rb <sub>20</sub>  [Ga <sub>20</sub> Ge <sub>20</sub> O <sub>80</sub> ]-THO			
	[Zn—Al—As—O]-THO			
	[Zn—P—O]-THO			
[Ga—Si—O]-THO				
UEI	*Tschörtnerite	3D	4.2 × 4.2, 5.6 × 3.1	Ring sizes - 8, 6, 4
UFI	*Mu-18	2D	3.5 × 4.6, 3.6 × 2.5	Ring sizes - 8, 6, 4
VNI	*UZM-5	2D	3.6 × 4.4, 3.2 × 3.2 (cage)	Ring sizes - 8, 6, 4
YUG	*VPI-9	3D	3.5 × 3.6, 3.1 × 4.0	Ring sizes - 8, 5, 4, 3
ZON	*Yugawaralite	2D	2.8 × 3.6, 3.1 × 5.0	Ring sizes - 8, 5, 4
ZON	Sr-Q	2D	2.5 × 5.1, 3.7 × 4.4	Ring sizes - 8, 6, 4
	*ZAPO-M1			
	GaPO-DAB-2 UjO-7			

[0040] Small pore zeolites with particular application for treating NO 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 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

TABLE 2-continued

Preferred small pore zeolites for use in treating exhaust gases of lean-burn internal combustion engines.	
Structure	Zeolite
ERI	SAPO-35 ZK-20 Erionite ZSM-34
	Linde type T
	Deca-dodecasil 3R
DDR	Sigma-1
	ZK-5
KFI	18-crown-6 [Zn—Ga—As—O]-KFI

TABLE 2-continued

Preferred small pore zeolites for use in treating exhaust gases of lean-burn internal combustion engines.	
Structure	Zeolite
EAB	TMA-E
PAU	ECR-18
MER	Merlinoite
AEI	SSZ-39
GOO	Goosecreekite
YUG	Yugawaralite
GIS	P1
VNI	VPI-9

**[0041]** 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.

**[0042]** The gas containing the nitrogen oxides can contact the zeolite catalyst at a gas hourly space velocity of from 5,000 hr<sup>-1</sup> to 500,000 hr<sup>-1</sup>, optionally from 10,000 hr<sup>-1</sup> to 200,000 hr<sup>-1</sup>.

**[0043]** 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).

**[0044]** Small pore zeolites for use in the invention can 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 zeolites for use in the present invention consist of zeolites having three-dimensional dimensionality. In another embodiment, the small pore zeolites for use in the present invention consist of zeolites having two-dimensional dimensionality.

**[0045]** In one embodiment, the at least one transition metal is selected from the group consisting of Cr, Ce, Mn, Fe, Co, Ni and Cu. In a preferred embodiment, the at least one transition metal is selected from the group consisting of Cu, Fe and Ce. In a particular embodiment, the at least one transition metal consists of Cu. In another particular embodiment, the at least one transition metal consists of Fe. In a further particular embodiment, the at least one transition metal is Cu and/or Fe.

**[0046]** The total of the at least one transition metal that can be included in the at least one transition metal-containing zeolite can be from 0.01 to 20 wt %, based on the total weight of the zeolite catalyst containing at least one transition metal. In one embodiment, the total of the at least one transition metal that can be included can be from 0.1 to 10 wt %. In a particular embodiment, the total of the at least one transition metal that can be included is from 0.5 to 5 wt %.

**[0047]** A preferred transition metal-containing two dimensional small pore zeolite for use in the present invention consists of Cu/LEV, such as Cu/Nu-3, whereas a preferred transition metal-containing three dimensional small pore zeo-

lite/aluminophosphate zeolite for use in the present invention consists of Cu/CHA, such as Cu/SAPO-34 or Cu/SSZ-13. In another embodiment, particularly where a ratio of NO/NO<sub>2</sub> is adjusted, e.g. by using a suitable oxidation catalyst (see hereinbelow) to about 1:1, Fe-containing zeolite catalysts are preferred, such as Fe-CHA, e.g. Fe/SAPO-34 or Fe/SSZ-13. Preliminary analysis indicates that Cu/SSZ-13 and Cu/Nu-3 are more resistant than the equivalent Cu/SAPO-34 to extended severe high temperature lean hydrothermal ageing (900° C. for 3 hours in 4.5% H<sub>2</sub>O/air mixture cf. Example 4).

**[0048]** 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.

**[0049]** The zeolite 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 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 zeolites for use in the present invention can be synthesized directly onto the substrate. Alternatively, the zeolite catalysts according to the invention can be formed into an extruded-type flow through catalyst.

**[0050]** The small pore zeolite catalyst containing at least one transition metal for use in the present invention is coated on a suitable monolith substrate. Washcoat compositions containing the zeolites 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 zeolite) silica-alumina, naturally occurring clays, TiO<sub>2</sub>, ZrO<sub>2</sub>, and SnO<sub>2</sub>.

**[0051]** In one embodiment, the nitrogen oxides are reduced with the reducing agent at a temperature of at least 100° C. In another embodiment, the nitrogen oxides are reduced with the reducing agent at a temperature from about 150° C. to 750° C. The latter embodiment 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.

**[0052]** In a particular embodiment, the temperature range is from 175 to 550° C. In another embodiment, the temperature range is from 175 to 400° C.

**[0053]** In another embodiment, the nitrogen oxides reduction is carried out in the presence of oxygen. In an alternative embodiment, the nitrogen oxides reduction is carried out in the absence of oxygen.

**[0054]** Zeolites for use in the present application include natural and synthetic zeolites, preferably synthetic zeolites 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<sub>2</sub>)<sub>2</sub>CO), ammonium carbonate, ammonium carbamate, ammonium hydrogen carbonate or ammonium formate.

[0056] The method can 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 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.

[0057] In a particular embodiment, the method is used for treating exhaust gas from a vehicular lean burn internal combustion engine, such as a diesel engine, a lean-burn gasoline engine or an engine powered by liquid petroleum gas or natural gas.

[0058] According to a further 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, a zeolite catalyst containing at least one transition metal disposed in a flow path of the exhaust gas and means for metering nitrogenous reductant into a flowing exhaust gas upstream of the zeolite catalyst, wherein the zeolite catalyst 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, Jr and Pt.

[0059] For the avoidance of doubt, the small pore transition metal-containing zeolites for use in the exhaust system aspect of the present invention include any for use in the method according to the invention as described hereinabove.

[0060] In one embodiment, the zeolite catalyst is 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., as described hereinabove. In another embodiment, the zeolite catalyst is formed into an extruded-type catalyst.

[0061] 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  $\text{NO}_x$  reduction at or above a desired efficiency, such as at above  $100^\circ\text{C}$ ., above  $150^\circ\text{C}$ . or above  $175^\circ\text{C}$ . 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.

[0062] 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  $\text{NO}_x$  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  $\text{NO}_x$  content of the exhaust gas.

[0063] The control means can comprise a pre-programmed processor such as an electronic control unit (ECU).

[0064] 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  $\text{NH}_3/\text{NO}$  and 4:3  $\text{NH}_3/\text{NO}_2$ .

[0065] In a further embodiment, an oxidation catalyst for oxidising nitrogen monoxide in the exhaust gas to nitrogen dioxide can be located upstream of a point of metering the nitrogenous reductant into the exhaust gas. In one embodiment, the oxidation catalyst is adapted to yield a gas stream entering the SCR zeolite catalyst having a ratio of  $\text{NO}$  to  $\text{NO}_2$  of from about 4:1 to about 1:3 by volume, e.g. at an exhaust gas temperature at oxidation catalyst inlet of  $250^\circ\text{C}$ . to  $450^\circ\text{C}$ . This concept is disclosed in S. Kasaoka et al. "Effect of Inlet  $\text{NO}/\text{NO}_2$  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.

[0066] The oxidation catalyst can include 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 aluminosilicate zeolite, silica, non-zeolite silica alumina, ceria, zirconia, titania or a mixed or composite oxide containing both ceria and zirconia.

[0067] 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.

[0068] 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.

[0069] In one embodiment, the control means meters nitrogenous reductant into the flowing exhaust gas only when the exhaust gas temperature is at least  $100^\circ\text{C}$ ., for example only when the exhaust gas temperature is from  $150^\circ\text{C}$ . to  $750^\circ\text{C}$ .

[0070] In a further aspect, there is provided a vehicular lean-burn engine comprising an exhaust system according to the present invention.

[0071] 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.

[0072] 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:

[0073] FIG. 1 is a graph showing  $\text{NO}$  conversion (at a gas hourly space velocity of  $30,000\text{ hr}^{-1}$ ) comparing transition metal-containing aluminosilicate catalysts with a transition metal-containing aluminophosphate/small pore zeolite catalyst after relatively moderate lean hydrothermal ageing performed on a laboratory reactor;

[0074] FIG. 2 is a graph showing  $\text{N}_2\text{O}$  formation in the test shown in FIG. 1;

[0075] FIG. 3 is a graph showing NO conversion (at a gas hourly space velocity of  $100,000 \text{ hr}^{-1}$ ) comparing Cu/Beta zeolite and Cu/SAPO-34 catalysts with a transition metal-containing aluminophosphate/small pore zeolite catalyst after relatively moderate lean hydrothermal ageing performed on a laboratory reactor;

[0076] FIG. 4 is a graph showing NO conversion (at a gas hourly space velocity of  $30,000 \text{ hr}^{-1}$ ) comparing transition metal-containing aluminosilicate catalysts with a transition metal-containing aluminophosphate/small pore zeolite catalyst after relatively severe lean hydrothermal ageing performed on a laboratory reactor;

[0077] FIG. 5 is a graph showing NO conversion for fresh Cu/Zeolite catalysts;

[0078] FIG. 6 is a graph showing NO conversion for aged Cu/Zeolite catalysts;

[0079] FIG. 7 is a graph showing  $\text{N}_2\text{O}$  formation for fresh Cu/Zeolite catalysts of FIG. 5;

[0080] FIG. 8 is a graph showing  $\text{N}_2\text{O}$  formation for aged Cu/Zeolite catalysts of FIG. 6;

[0081] FIG. 9 is a graph showing the effect of adding HC species to Cu/zeolite catalysts during  $\text{NH}_3$  SCR at  $300^\circ \text{C}$ .;

[0082] FIG. 10 is a graph showing hydrocarbon breakthrough following addition of hydrocarbon species to Cu/zeolite catalysts during  $\text{NH}_3$  SCR at  $300^\circ \text{C}$ .;

[0083] FIG. 11 is a graph showing the adsorption profiles of n-octane at  $150^\circ \text{C}$ . flowing through the Cu zeolite catalysts;

[0084] FIG. 12 is a graph of the temperature programmed desorption (TPD) of HC species to Cu/zeolite catalysts after HC adsorption at  $150^\circ \text{C}$ .;

[0085] FIG. 13 is a graph similar to FIG. 6 comparing NO conversion activity for aged Cu/Sigma-1, Cu-SAPO-34, Cu/SSZ-13 and Cu/Beta;

[0086] FIG. 14 is a graph similar to FIG. 8 comparing  $\text{N}_2\text{O}$  formation for the aged Cu/zeolite catalysts of FIG. 13;

[0087] FIG. 15 is a graph similar to FIG. 13 comparing NO conversion activity for aged Cu/ZSM-34, Cu/SAPO-34, Cu/SSZ-13 and Cu/Beta catalysts;

[0088] FIG. 16 is a graph comparing the NO conversion activity of fresh and aged Cu-SAPO-34 and Cu/SSZ-13 catalysts;

[0089] FIG. 17 is a graph comparing the NO conversion activity of fresh samples of Cu/SAPO-34 with a Cu/naturally occurring chabazite type material;

[0090] FIG. 18 is a bar chart comparing the NO conversion activity of fresh Cu/SAPO-34 with that of two fresh Cu/naturally occurring chabazite type materials at two temperature data points;

[0091] FIG. 19 is a bar chart comparing the NO conversion activity of aged Cu/Beta, Cu/SAPO-34, Fe/SAPO-34 and Fe/SSZ-13 catalysts at two temperature data points;

[0092] FIG. 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;

[0093] FIG. 21 is a graph showing hydrocarbon breakthrough following the introduction of n-octane in the experiment of FIG. 20;

[0094] FIG. 22 is a bar chart comparing the effect on NO conversion activity for a fresh Fe/SSZ-13 catalyst of using 100% NO as a component of the feed gas with using 1:1 NO: $\text{NO}_2$ ;

[0095] FIG. 23 is a schematic diagram of an embodiment of an exhaust system according to the present invention.

[0096] FIG. 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.

[0097] An iron/small pore zeolite SCR catalyst 20 also coated on a ceramic flow-through substrate monolith is disposed downstream of the wall-flow filter 18. An  $\text{NH}_3$  oxidation clean-up or slip catalyst 21 is coated on a downstream end of the SCR catalyst monolith substrate. Alternatively, the  $\text{NH}_3$  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 sensor 32 located downstream of the SCR catalyst.

[0098] In use, the oxidation catalyst 16 passively oxidises NO to  $\text{NO}_2$ , particulate matter is trapped on filter 18 and is combusted in  $\text{NO}_2$ . NO 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  $\text{NO}_2$  in the total NO content of the exhaust gas entering the SCR catalyst (about 1:1) are desirable for NO reduction on a SCR catalyst as they are more readily reduced to  $\text{N}_2$ . The  $\text{NH}_3$  slip catalyst 21 oxidises  $\text{NH}_3$  that would otherwise be exhausted to atmosphere. A similar arrangement is described in WO 99/39809.

## EXAMPLES

### Example 1

Method of Making Fresh 5 wt % Fe/Beta or SAPO-34 or 3 wt % SSZ-13 Zeolite Catalyst

[0099] Commercially available Beta zeolite, SAPO-34 or SSZ-13 was  $\text{NH}_4^+$  ion exchanged in a solution of  $\text{NH}_4\text{NO}_3$ , then filtered. The resulting material was added to an aqueous solution of  $\text{Fe}(\text{NO}_3)_3$  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 3 wt % Cu/Aeolites

[0100] Commercially available SAPO-34, SSZ-13, Sigma-1, ZSM-34, Nu-3, ZSM-5 and Beta zeolites were  $\text{NH}_4^+$  ion exchanged in a solution of  $\text{NH}_4\text{NO}_3$ , then filtered. The resulting materials were added to an aqueous solution of  $\text{Cu}(\text{NO}_3)_2$  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

**[0101]** The catalysts obtained by means of Examples 1 and 2 were lean hydrothermally aged at 750° C. for 24 hours in 4.5% H<sub>2</sub>O/air mixture.

## Example 4

## Severe Lean Hydrothermal Ageing

**[0102]** 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<sub>2</sub>O/air mixture.

## Example 5

## Extended Severe Lean Hydrothermal Ageing

**[0103]** 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<sub>2</sub>O/air mixture.

## Example 6

## Test Conditions

**[0104]** Separate samples of Fe/BetaBeta prepared according to Example 1 and Cu/BetaBeta, Cu/ZSM-5 and Cu/SAPO-34 prepared according to Example 2 were aged according to Examples 3 and 4 and tested in a laboratory apparatus using the following gas mixture: 350 ppm NO, 350 ppm NH<sub>3</sub>, 14% O<sub>2</sub>, 4.5% H<sub>2</sub>O, 4.5% CO<sub>2</sub>, N<sub>2</sub> balance. The results are shown in FIGS. 1 to 4 inclusive.

**[0105]** Tests were also conducted on Cu/BetaBeta, Cu/ZSM-5, Cu/SAPO-34 and Cu/Nu-3 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<sub>2</sub> was used. The results are shown in FIGS. 5 to 8 inclusive.

## Example 7

## n-Octane Adsorption Test Conditions

**[0106]** With the catalyst loaded in a laboratory apparatus, 1000 ppm (as Cl equivalents) propene, n-octane or toluene was injected during NH<sub>3</sub> SCR at 300° C. (350 ppm NO, 350 ppm NH<sub>3</sub>, 12% O<sub>2</sub>, 4.5% H<sub>2</sub>O, 4.5% CO<sub>2</sub>, balance N<sub>2</sub>). Hydrocarbon desorption was measured by ramping the temperature at 10° C./minute in 12% O<sub>2</sub>, 4.5% H<sub>2</sub>O, 4.5% CO<sub>2</sub>, balance N<sub>2</sub>.

## Example 8

## Results for Experiments Shown in FIGS. 1 to 4 Inclusive

**[0107]** FIG. 1 compares the NO 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 with NH<sub>3</sub>.

**[0108]** FIG. 2 compares the N<sub>2</sub>O formation over the catalysts. It is clear that the Cu/SAPO-34 catalyst produced lower levels of N<sub>2</sub>O compared to the other two Cu-containing catalysts. The Fe-containing catalyst also exhibits low N<sub>2</sub>O formation, but as shown in FIG. 1, the Fe catalyst is less active at lower temperatures.

**[0109]** FIG. 3 compares the NO 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.

**[0110]** FIG. 4 shows the NO 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 FIGS. 5 to 12 Inclusive

**[0111]** NH<sub>3</sub> 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 FIG. 5. The corresponding activity for the same catalysts aged under severe lean hydrothermal conditions is shown in FIG. 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.

**[0112]** The N<sub>2</sub>O formation measured for the fresh and aged catalysts is shown in FIGS. 7 and 8, respectively. The results clearly show that N<sub>2</sub>O formation is significantly reduced by means of supporting Cu on zeolites that do not have large pores.

**[0113]** FIG. 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<sub>3</sub> SCR reaction at 300° C. FIG. 10 shows the corresponding HC breakthrough following HC addition.

**[0114]** FIG. 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. FIG. 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 FIGS. 13 and 14

**[0115]** 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 FIG. 13, from which it can be seen that the NO 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 FIG. 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 FIG. 15

[0116] 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 FIG. 15, from which it can be seen that the NO 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 FIG. 16

[0117] 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 FIG. 16, from which it can be seen that the NO conversion activity of Cu/SSZ-13 is maintained even after extended severe lean hydrothermal ageing.

#### Example 13

##### Results for Experiments Shown in FIGS. 17 and 18

[0118] 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 FIG. 17, from which it can be seen that the NO conversion activity of the naturally occurring Cu/chabazite is significantly lower than Cu/SAPO-34. FIG. 18 is a bar chart comparing the NO 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 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 FIG. 19

[0119] 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 activity at the 350° C. and 450° C. data points is shown in FIG. 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 FIGS. 20 and 21

[0120] 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 a exhaust gas) was introduced at 8 minutes into the test. The results shown in FIG. 20 compare the NO<sub>x</sub> 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.

[0121] The hypothesis that coking of the Fe/Beta catalyst is responsible for the dramatic reduction of NO conversion activity is reinforced by the results shown in FIG. 21, wherein Cl 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 Cl hydrocarbon is observed in the effluent for the Fe/Beta sample. Since there is significantly less Cl 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<sub>x</sub> conversion activity.

#### Example 16

##### Results for Experiments Shown in FIG. 22

[0122] 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 350 ppm NO was replaced with a mixture of 175 ppm NO and 175 ppm NO<sub>2</sub>, i.e. 350 ppm total NO<sub>x</sub>. The results from both tests are shown in FIG. 22, from which the significant improvement obtainable from increasing the NO<sub>2</sub> content of NO in the feed gas to 1:1 can be seen. In practice, the NO:NO<sub>2</sub> 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<sub>3</sub>-SCR catalyst.

1. A catalyst for treating exhaust gas comprising at least one small pore molecular sieve having an KFI framework and containing from 0.01 to 20 weight percent of a metal selected from the group consisting of Cr, Mn, Fe, Co, Ce, Ni, Cu, Zn, Ga, Mo, Ru, Rh, Pd, Ag, In, Sn, Re, Jr and Pt and combinations thereof, based on the total weight of the molecular sieve.

2. The catalyst of claim 1, wherein said molecular sieve has silica-to-alumina ratio (SAR) of 2 to 300.

3. The catalyst of claim 1, wherein said molecular sieve has an isotype selected from ZK-5, 118-crown-61[Al—Si—O]-KFI, [Zn—Ga,As—O]-KFI, (Cs,K)-ZK-5, P, and Q isotypes.

4. The catalyst of claim 1, wherein said molecular sieve is a ZK-5 isotype.

5. The catalyst of claim 1, wherein said metal is copper.

6. The catalyst of claim 1, wherein said metal is platinum.

7. The catalyst of claim 1, wherein said molecular sieve is an aluminosilicate and has an SAR of 8 to 150.

8. The catalyst of claim 1, wherein said transition metal is present in an amount of 0.5 to 5 wt. % based on the total weight of the molecular sieve.

9. The catalyst of claim 1, wherein said transition metal is added to the zeolite by one of incipient wetness, ion exchange, and during zeolite synthesis.

10. The catalyst of claim 1, further comprising a metal promoted medium, large, or meso-pore molecular sieve.

11. The catalyst of claim 1, further comprising a Cu or Fe promoted molecular sieve having a chabazite framework.

12. A catalytic washcoat comprising a catalyst according to any of claims 1, and further comprising at least one binder

selected from alumina, silica, non-zeolite silica-alumina, natural clay,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{SnO}_2$ .

**13.** A catalytic article comprising a washcoat according to claim **12** coated on a substrate selected from a metal flow-through substrate, a ceramic flow-through substrate, a wall-flow filter, a sintered metal filter, and a partial filter.

**14.** A catalytic article comprising an extruded-type flow through honeycomb formed from an extrudate comprising a catalyst according to claim **1**.

**15.** The catalytic article of claim **14** further comprising a transition metal promoted zeolite coating.

**16.** A system for treating exhaust gas comprising a selective catalytic reduction (SCR) catalyst upstream of an  $\text{NH}_3$  oxidation catalyst (AMOX), wherein in at least one of said SCR and AMOX catalysts comprise a catalyst according to claim **1**.

**17.** The system of claim **16** further comprising a catalyzed soot filter and a diesel oxidation catalyst having a platinum

group metal, wherein said diesel oxidation catalyst is disposed upstream of said selective catalytic reduction catalyst.

**18.** A method for treating an exhaust gas comprising the steps of:

- a. contacting an exhaust gas stream containing  $\text{NO}_x$  and/or  $\text{NH}_3$  in the presence of a catalyst according to claim **1**; and
- b. converting at least a portion of said  $\text{NO}$  to  $\text{N}_2$  and/or converting at least a portion of  $\text{NH}_3$  to at least one of  $\text{N}_2$  and  $\text{NO}_2$ .

**19.** The method of claim **18**, wherein said exhaust gas contains  $\text{NO}_x$ , a nitrogenous reducing agent, and a ratio of  $\text{NO}$  to  $\text{NO}_2$  from about 4:1 to about 1:3 by volume, and said catalyst is a selective reduction catalyst.

**20.** The method of claim **18**, wherein said exhaust gas contains  $\text{NH}_3$  and said catalyst is an ammonia slip catalyst.

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