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(54) Benævnelse: **SCR-fremgangsmåde og system ned Cu/sapo-34 zeolitkatalysator**

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DESCRIPTION

[0001] 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.

[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).

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

[0005] Also, side reactions may lead to undesirable products such as N_2O, as represented by reaction (3).

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

[0006] 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.

[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_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.

[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_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.

[0010] 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.

[0011] 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.

[0012] 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)).

[0013] 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.

[0014] 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.

[0015] WO 2004/002611 discloses an NH_3-SCR catalyst comprising a ceria-doped aluminosilicate zeolite.

[0016] 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.

[0017] 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.

[0018] 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.

[0019] 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.

[0020] 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.

[0021] 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.

[0022] DE 10 2005 010 221 discloses a catalytically active metal exchanged natural tectosilicate for treating exhaust gases, particularly of automobiles. Copper and/or iron is preferred as the exchanging metal. The natural tectosilicate can include, among others, natural chabazite. Hydrocarbons, aqueous or solid urea can be used as a reductant. As a specific Example, a catalyst comprising a blend of natural clinoptilolite and heulandite is provided but without mentioning the exchanged metal or reductant used.

[0023] DE 10 2004 013 164 discloses a catalyst for purifying NO_x in the exhaust gas of motor vehicles, which catalyst comprising modified clay minerals selected from the group consisting of bentonites, smectites, hectorites and mixtures thereof, all of which being pillared with aluminium, silicon or titanium (oxides). In an embodiment, a preferred catalyst contains at least one oxidative region for oxidising NO, which contains e.g. zeolites, and a reductive region formed by the clay minerals. The zeolites include, among others, chabasite. Hydrocarbons are used as reducing agent. The hydrocarbons are able to pass the zeolite oxidative region unoxidised for reaction on the downstream reductive region. The catalyst can contain oxidative-acting metal ions.

[0024] WO 2008/106519 was filed earlier but published after the filing date of the present application. According to the abstract, it discloses zeolite catalysts, systems and methods for preparing and using zeolite catalysts having the CHA crystal structure. The catalysts are said to be useful for removing nitrogen oxides from a gaseous medium across a broad temperature range and of exhibiting hydrothermal stability at high reaction temperatures. The zeolite catalysts disclosed include a zeolite carrier having a silica to alumina ratio from about 15:1 to about 256:1 and a copper to alumina ratio from about 0.25:1 to about 1:1.

[0025] WO 2008/118434 was filed earlier but published after the filing date of the present application. It 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 micropore 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 vapour for a time ranging from 1 to 16 hours. Methods of using the disclosed crystalline material, such as in the selective catalytic reduction of NOx in exhaust gas are also disclosed, as are methods of making such materials. The document discloses that any suitable physical form of the catalyst may be utilized, including, but not limited to: a channelled or honeycombed-type body; a packed bed of balls, pebbles, pellets, tablets, extrudates or other particles; microspheres; and structural pieces, such as plates or tubes.

[0026] 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.

[0027] 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, which zeolite catalyst is coated on a monolith substrate, wherein the zeolite is a small pore zeolite containing a maximum ring size of eight tetrahedral atoms, wherein the zeolite has the CHA Framework Type Code, wherein the CHA Framework Type Code

zeolite is SAPO-34 and wherein the at least one transition metal is Cu.

[0028] 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.

[0029] 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). 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, 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.

[0030] 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 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).

[0031] The zeolite catalysts for use in the present invention are coated on a suitable substrate monolith.

[0032] It will be appreciated that the invention extends to catalyst coatings comprising both Cu-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 zeolite catalysts *per se* as described herein. It should also be understood that the catalyst coatings for use in the invention can comprise combinations of two or more transition metal-containing small pore zeolites, one of which according to the invention.

[0033] In this invention, we have discovered that certain 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. The small pore zeolite for use in the present invention is SAPO-34, which is an aluminophosphate zeolite.

[0034] 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).

[0035] We believe that the claimed small pore zeolite catalysts 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 (2.6A) is smaller than those of the typical hydrocarbons (C_3H_6 ~ 4.5Å, n-C_8H_{18} ~4.3Å and C_7H_8 ~ 6.0Å) present in, for example, diesel engine exhaust. 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. Details of the small pore zeolite for use in the present invention 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)	Isotypic framework structure according to the invention	Dimensionality	Pore size (Å)	Additional info
CHA	SAPO-34	3D	3.8 x 3.8	Ring sizes - 8, 6, 4

[0036] Small pore zeolites according to the invention have particular application for treating NO_x in exhaust gases of lean-burn internal combustion engines, e.g. vehicular exhaust gases. 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.

[0037] 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}.

[0038] Zeolites of the Framework Type Code CHA have three-dimensional dimensionality.

[0039] 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%.

[0040] 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.

[0041] The zeolite catalyst for use in the present invention is 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.

[0042] 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 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.

[0043] 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.

[0044] 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.

[0045] 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.

[0046] Zeolites for use in the present application are synthetic zeolites and have a more uniform: silica-to-alumina ratio (SAR), crystallite size, crystallite morphology, and the absence of impurities (e.g. alkaline earth metals).

[0047] 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.

[0048] 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.

[0049] 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.

[0050] 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, which zeolite catalyst is coated on a monolith substrate and is 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 zeolite has the CHA Framework Type Code, wherein the CHA Framework Type Code zeolite is SAPO-34 and wherein the at least one transition metal is Cu.

[0051] For the avoidance of doubt, the small pore transition metal-containing zeolites for use in the exhaust system aspect of the present invention include that for use in the method according to the invention as described hereinabove.

[0052] 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.

[0053] 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.

[0054] 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.

[0055] The control means can comprise a pre-programmed processor such as an electronic control unit (ECU).

[0056] 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.

[0057] 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 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.

[0058] 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.

[0059] 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.

[0060] 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.

[0061] 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.

[0062] In a further aspect, there is provided a vehicular lean-burn engine comprising an exhaust system according to the present invention.

[0063] 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.

[0064] 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 aluminosilicate catalysts (comparative) with a transition metal-containing aluminophosphate/small pore zeolite catalyst (of 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 (comparative) and Cu/SAPO-34 (of the invention) catalysts 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 aluminosilicate catalysts (comparative) with a transition metal-containing aluminophosphate/small pore zeolite catalyst (of 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 (of the invention and comparative);

Figure 6 is a graph showing NO_X conversion for aged Cu/Zeolite catalysts (of the invention and comparative);

Figure 7 is a graph showing N_2O formation for fresh Cu/Zeolite catalysts of Figure 5;

Figure 8 is a graph showing N_2O formation for aged Cu/Zeolite catalysts of Figure 6;

Figure 9 is a graph showing the effect of adding HC species to Cu/zeolite catalysts (of the invention and comparative) during NH_3 SCR at 300°C;

Figure 10 is a graph showing hydrocarbon breakthrough following addition of hydrocarbon species to Cu/zeolite catalysts (of the invention and comparative) during NH_3 SCR at 300°C;

Figure 11 is a graph showing the adsorption profiles of n-octane at 150°C flowing through Cu zeolite catalysts (of the invention and comparative);

Figure 12 is a graph of the temperature programmed desorption (TPD) of HC species to Cu/zeolite catalysts (of the invention and comparative) 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;

Figure 14 is a graph similar to Figure 8 comparing N_2O formation for the aged Cu/zeolite catalysts 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;

Figure 16 is a graph comparing the NO_x conversion activity of fresh and aged Cu-SAPO-34 and Cu/SSZ-13 catalysts;

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;

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 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 at two temperature data points;

Figure 20 is a schematic diagram of an embodiment of an exhaust system illustrating the present invention. While the catalyst in the embodiment is not according to the invention, the skilled person will understand how the system may be adapted for use with catalysts according to the invention.

Figure 20 is a schematic diagram of an embodiment of an exhaust system for use in the present invention, wherein diesel engine 12 comprises an exhaust system 10 for use in 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.

[0065] 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 NH_3 oxidation cleanup 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.

[0066] 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

Comparative Example 1 - Method of making fresh 5wt%Fe/Beta or SAPO-34 or 3wt%SSZ-13 zeolite catalyst

[0067] 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 (comparative and according to the invention)

[0068] Commercially available SAPO-34, SSZ-13, Sigma-1, ZSM-34, Nu-3, ZSM-5 and Beta zeolites 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

[0069] The catalysts obtained by means of Comparative Example 1 and Example 2 were lean hydrothermally aged at 750°C for 24 hours in 4.5% H_2O/air mixture.

Example 4 - Severe Lean Hydrothermal Ageing

[0070] The catalysts obtained by means of Comparative Example 1 and Example 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

[0071] The catalysts obtained by means of Comparative Example 1 and Example 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

[0072] Separate samples of Fe/Beta prepared according to Comparative Example 1 and Cu/Beta (comparative), Cu/ZSM-5 (comparative) and Cu/SAPO-34 (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.

[0073] Tests were also conducted on Cu/Beta (comparative), Cu/ZSM-5 (comparative), Cu/SAPO-34 (according to the invention) and Cu/Nu-3 (comparative) 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

[0074] 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

[0075] Figure 1 compares the NO_x reduction efficiencies of a Cu/SAPO-34 catalyst (according to the invention) against a series of aluminosilicate zeolite supported transition metal catalysts (Cu/ZSM-5, Cu/Beta and Fe/Beta - all comparative) 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.

[0076] 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.

[0077] 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.

[0078] 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

[0079] NH_3 SCR activity of fresh (i.e. un-aged) Cu supported on the small pore zeolites SAPO-34 (according to the invention) and Nu-3 (comparative) 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.

[0080] 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.

[0081] Figure 9 compares the effect of HC on Cu/zeolite catalysts where SAPO-34 is according to the invention. For comparison, Nu-3, ZSM-5 and Beta zeolite are used as examples of a small, 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.

[0082] 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 (according to the invention) and Nu-3 (comparative), 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

[0083] Cu/SSZ-13 (comparative), Cu/SAPO-34 (according to the invention), Cu/Sigma-1 (comparative) and Cu/Beta (comparative) 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

[0084] Cu/ZSM-34 (comparative), Cu/SAPO-34 (according to the invention), Cu/SSZ-13 (comparative) and Cu/Beta (comparative) 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

[0085] Fresh samples of Cu/SSZ-13 (comparative) and Cu/SAPO-34 (according to the invention) 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

[0086] Cu/SAPO-34 (according to the invention) and a Cu/naturally occurring chabazite-type material (comparative) 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 Cu/naturally occurring 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

[0087] Cu/SAPO-34 (according to the invention) and Cu/Beta (comparative) were prepared according to Example 2. Fe/SAPO-34 (comparative) and Fe/SSZ-13 (comparative) were prepared according to Comparative 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.

REFERENCES CITED IN THE DESCRIPTION

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P A T E N T K R A V

1. Fremgangsmåde til omdannelse af nitrogenoxider i en gas til nitrogen ved at bringe nitrogenoxiderne i kontakt med et nitrogenholdigt reduktionsmiddel under tilstedeværelsen af en zeolitkatalysator, der indeholder mindst ét overgangsmetal, hvor zeolitkatalysatoren er coatet på et monolit substrat, hvor zeolitten er en småporet zeolit indeholdende en maksimal ringstørrelse på otte tetraediske atomer, hvor zeolitten har en CHA Framework-Type-Code, hvor CHA Framework-Type-Code zeolitten er SAPO-34, og hvor det mindst éne overgangsmetal er Cu.

2. Fremgangsmåde ifølge krav 1, hvor det samlede mindst éne overgangsmetal foreliggende i katalysatoren udgør fra 0,01 til 20 vægt%, baseret på den samlede vægt af zeolitkatalysatoren.

3. Fremgangsmåde ifølge krav 1 eller 2, hvor nitrogenoxiderne reduceres med reduktionsmidlet ved en temperatur på mindst 100°C.

4. Fremgangsmåde ifølge krav 1, 2 eller 3, hvor reduktionen af nitrogenoxiderne udføres under tilstedeværelse af oxygen.

5. Fremgangsmåde ifølge et hvilket som helst foregående krav, hvor tilførsel af nitrogenholdigt reduktionsmiddel er styret således, at NH_3 ved zeolitkatalysatorindløbet er styret til at være 60% til 200% af teoretisk ammoniak udregnet ved 1:1 NH_3/NO og 4:3 NH_3/NO_2.

6. Fremgangsmåde ifølge et hvilket som helst foregående krav, hvor nitrogenmonoxid i gassen oxideres til nitrogendioxid ved anvendelse af en oxidationskatalysator anbragt opstrøms af zeolitkatalysatoren, og den fremkomne gas derefter blandes med nitrogenholdigt reduktionsmiddel før blandingen fødes ind i zeolitkatalysatoren, hvor oxidationskatalysatoren er tilpasset til at tilvejebringe en gasstrøm, der trænger ind i zeolitkatalysatoren, som har en ratio af NO til NO_2 af fra omkring 4:1 til omkring 1:3 efter volumen.

7. Fremgangsmåde ifølge et hvilket som helst foregående krav, hvor gassen som indeholder nitrogenoxider er afledt fra en forbrændingsprocess.

8. Fremgangsmåde ifølge krav 7, hvor forbrændingsprocessen er forbrændingen af brændstof i en køretøjsmotor med mager indre forbrænding.

9. Fremgangsmåde ifølge et hvilket som helst foregående krav, hvor det monolitte substrat er et monolit gennemstrømssubstrat eller et monolit filtersubstrat.

10. Fremgangsmåde ifølge krav 9, hvor det monolitte filtersubstrat er et vægstrømsfilter (ENG: wall-flow filter).

11. Udstødningssystem til en køretøjsmotor med mager indre forbrænding, systemet omfatter en rørledning til at bære en strømmende udstødningsgas, en kilde af nitrogenholdigt reduktionsmiddel, en zeolitkatalysator indeholdende mindst ét overgangsmetal, zeolitkatalysatoren er coatet på et monolitsubstrat og er anordnet i en strømningsvej af udstødningsgassen, og middel til dosering af nitrogenholdigt reduktionsmiddel ind i en strømmende udstødningsgas, opstrøms af zeolitkatalysatoren, hvor zeolitkatalysatoren er en småporet zeolit indeholdende en maksimal ringstørrelse på otte tetraediske atomer, hvor

zeolitten har en CHA Framework-Type-Code, hvor CHA Framework-Type-Code zeolitten er SAPO-34, og hvor det mindst éne overgangsmetal er Cu.

12. Udstødningssystem ifølge krav 11, hvor zeolitkatalysatoren er coatet på et monolit gennemstrømssubstrat eller et monolit filtersubstrat.

13. Udstødningssystem ifølge krav 12, hvor det monolitte filtersubstrat er et vægstrømsfilter (ENG: wall-flow filter).

14. Udstødningssystem ifølge krav 11, 12 eller 13, omfattende midler, når i anvendelse, til styring af doseringsmidlet således at nitrogenholdigt reduktionsmiddel doseres ind i den strømmende udstødningsgas kun når det bestemmes at zeolitkatalysatoren er i stand til at katalysere NO_x reduktion ved eller over en efterstræbt effektivitet.

15. Udstødningssystem ifølge et hvilket som helst af krav 11 til 14, hvor en oxidationskatalysator til oxidation af nitrogenmonoxid til nitrogendioxid er lokaliseret opstrøms af midlet til dosering af nitrogenholdigt reduktionsmiddel ind i en strømmende udstødningsgas.

16. Udstødningssystem ifølge et hvilket som helst af krav 11 til 15, hvor et filtersubstrat er anbragt mellem oxidationskatalysatoren og zeolitkatalysatoren.

17. Apparat omfattende mager køretøjsmotor og et udstødningssystem ifølge et hvilket som helst af krav 11 til 16.

18. Apparat ifølge krav 17, hvor motoren er en dieselmotor, en mager benzinmotor eller en motor drevet af flydende petroleumsgas eller naturlig gas.

DRAWINGS

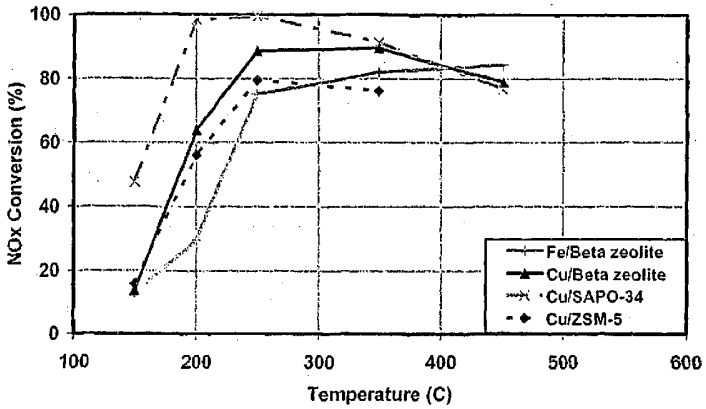


FIGURE 1

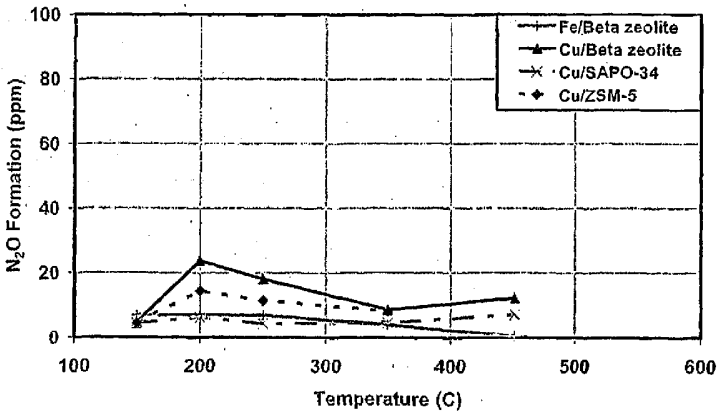


FIGURE 2

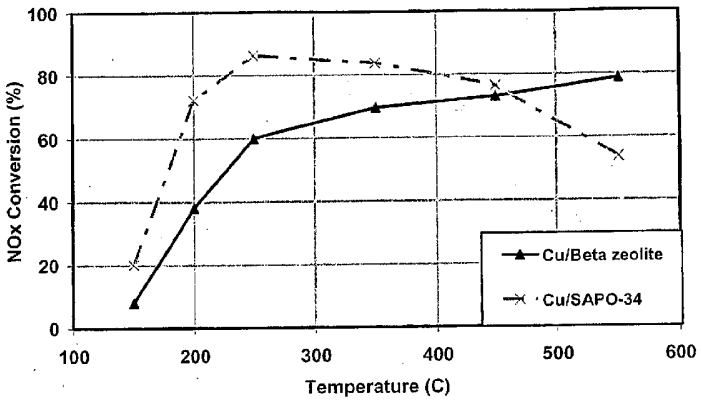


FIGURE 3

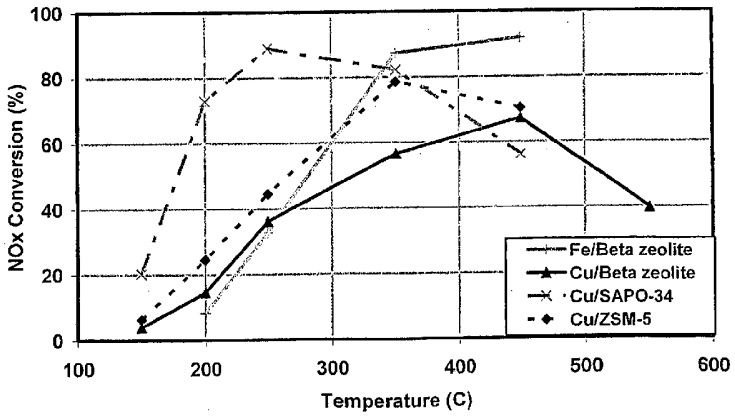


FIGURE 4

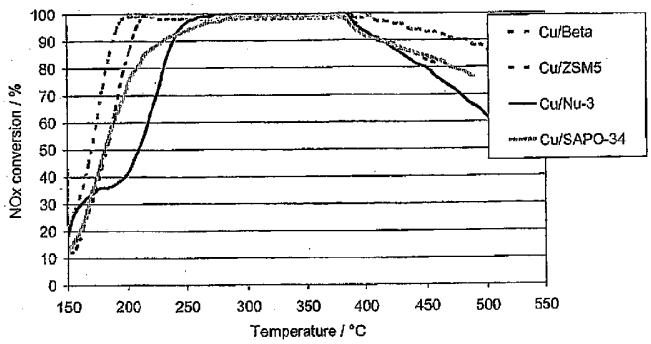


FIGURE 5

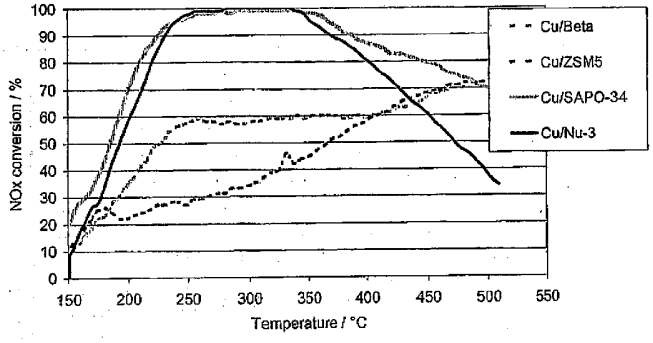


FIGURE 6

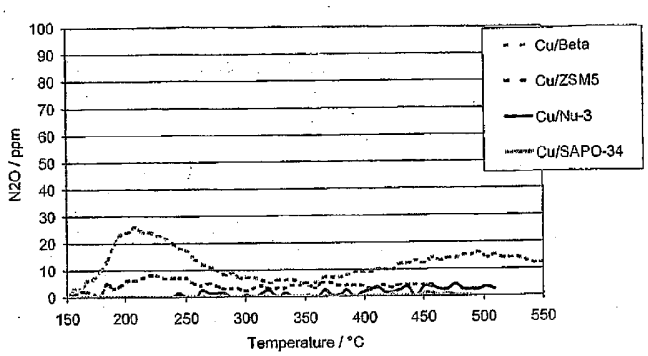


FIGURE 7

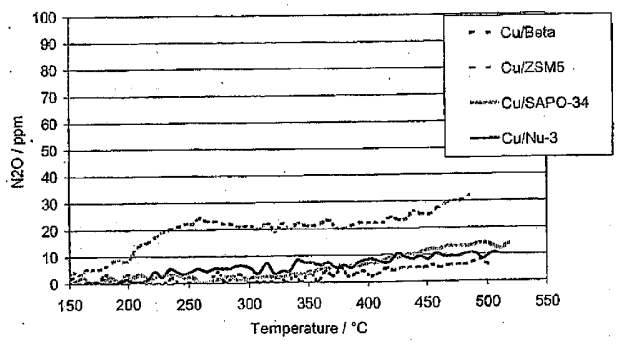


FIGURE 8

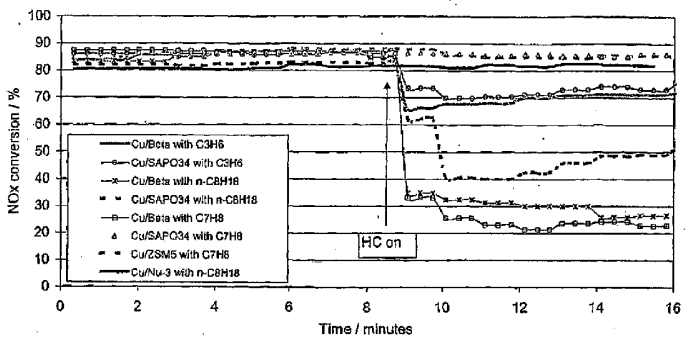


FIGURE 9

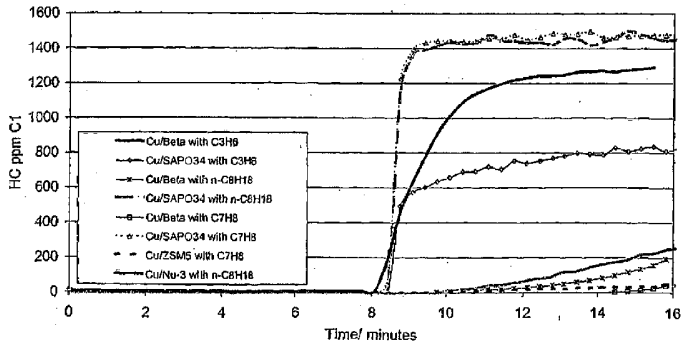


FIGURE 10

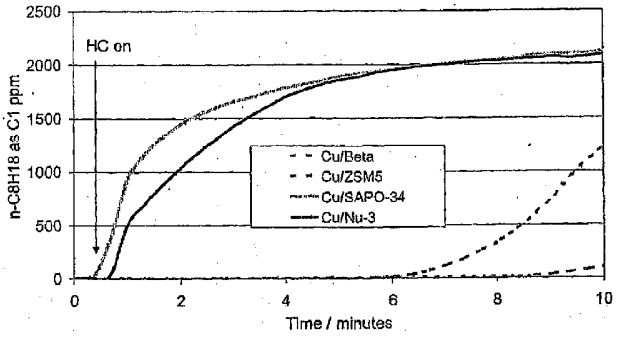


FIGURE 11

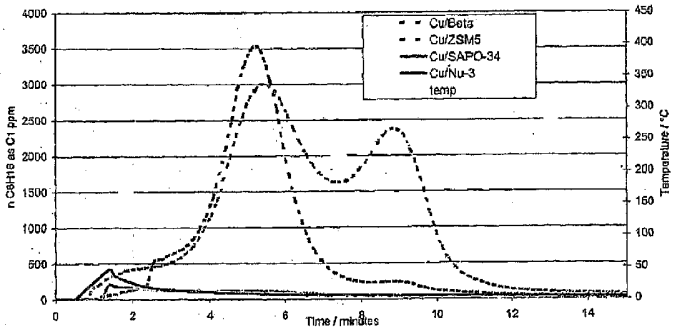


FIGURE 12

Figure 13

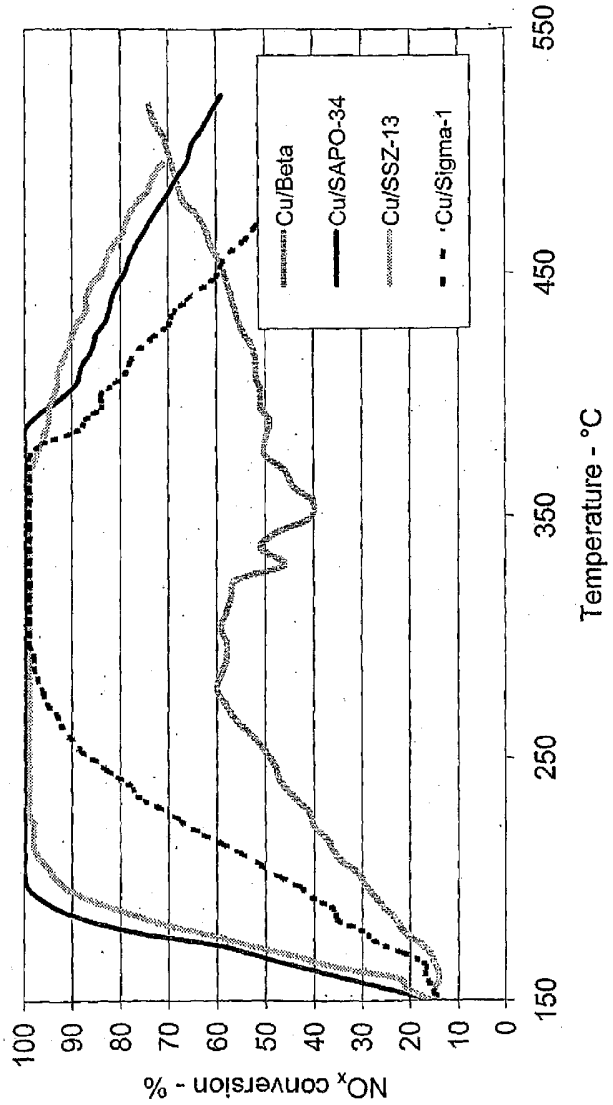

Cu/Beta
Cu/SAPO-34
Cu/SSZ-13
Cu/Sigma-1
NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
150
250
350
450
550
Temperature - °C

Figure 14

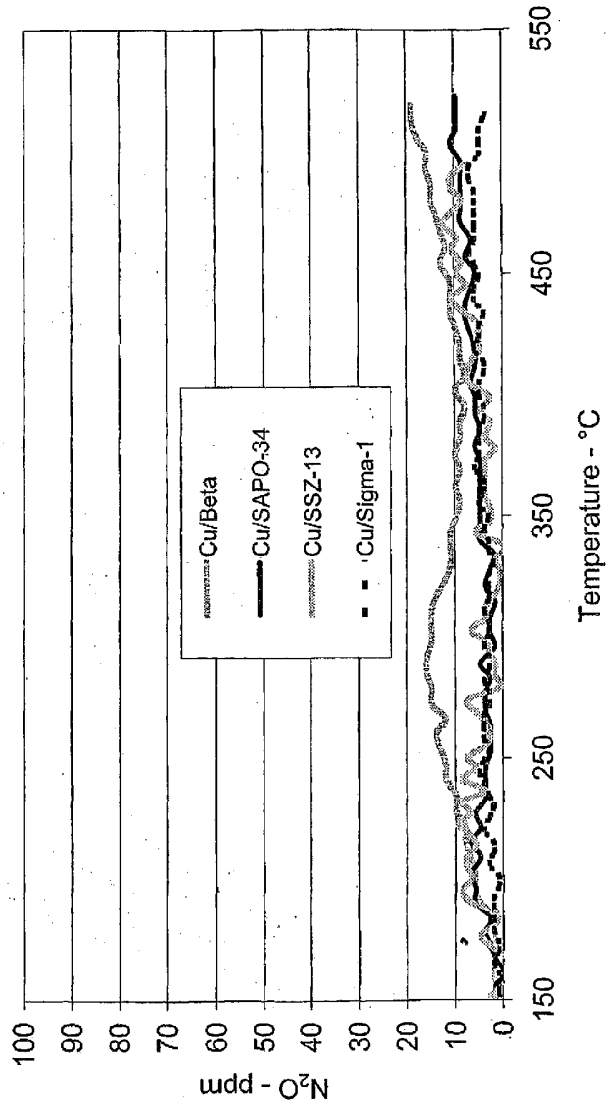

Cu/Beta
Cu/SAPO-34
Cu/SSZ-13
Cu/Sigma-1
N2O - ppm
100
90
80
70
60
50
40
30
20
10
0
150
250
350
450
550
Temperature - °C

Figure 15

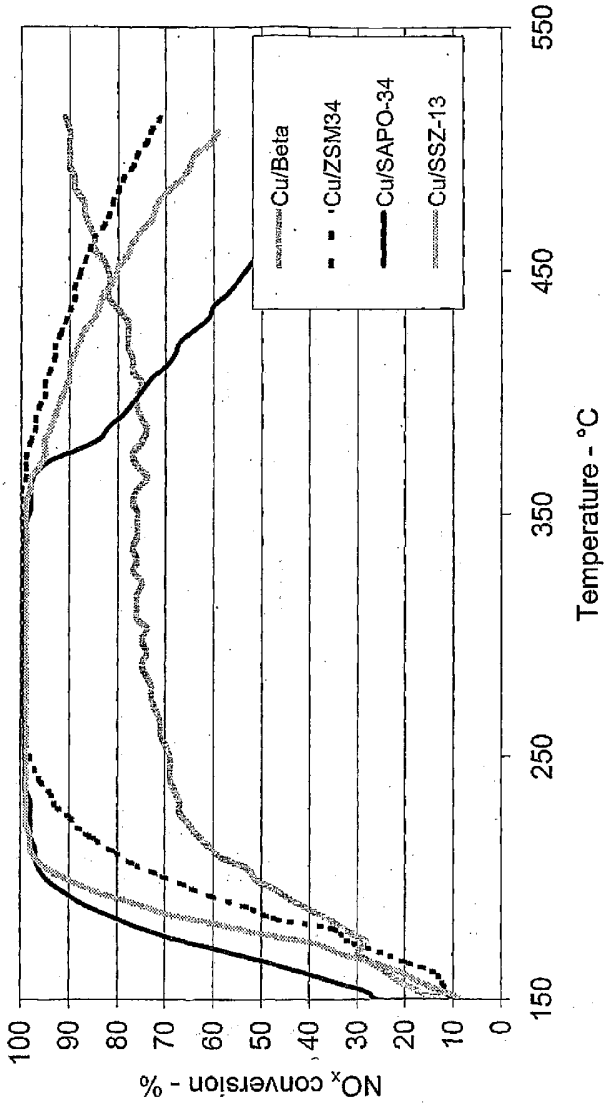

NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
150
250
350
450
550
Temperature - °C
Cu/Beta
Cu/ZSM34
Cu/SAPO-34
Cu/SSZ-13

Figure 1a

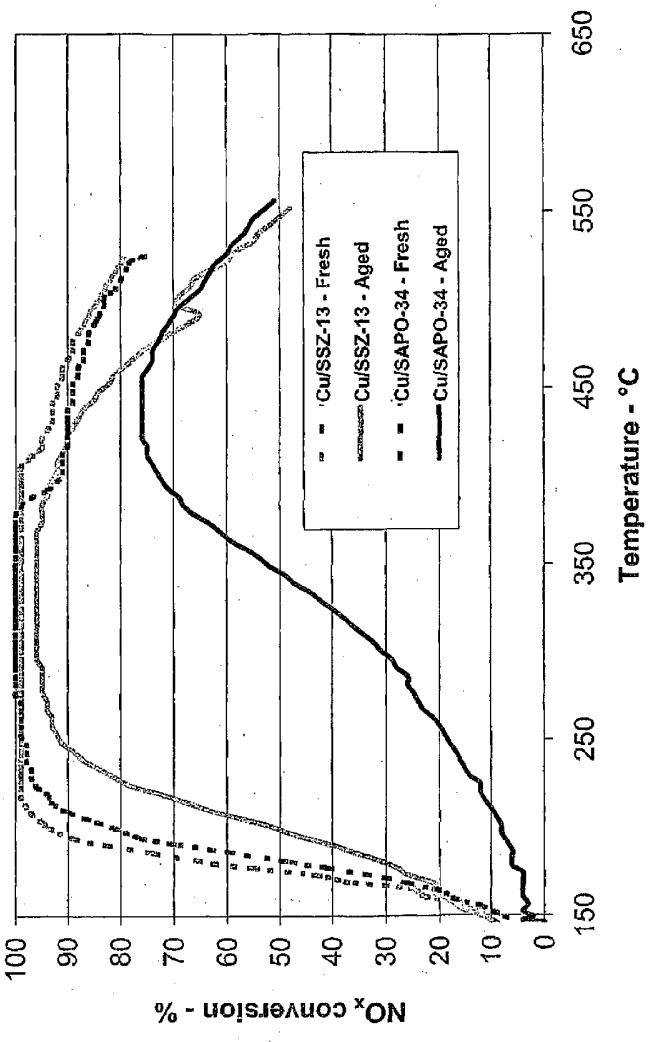
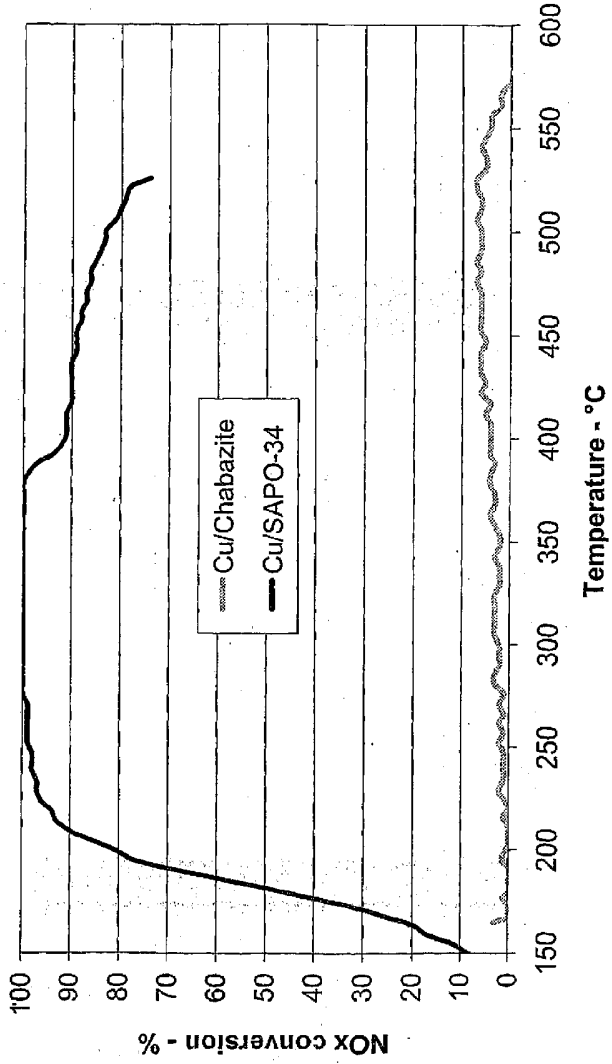

Cu/SSZ-13 - Fresh
Cu/SSZ-13 - Aged
Cu/SAPO-34 - Fresh
Cu/SAPO-34 - Aged
NOx conversion - %
Temperature - °C
0
10
20
30
40
50
60
70
80
90
100
150
250
350
450
550
650

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

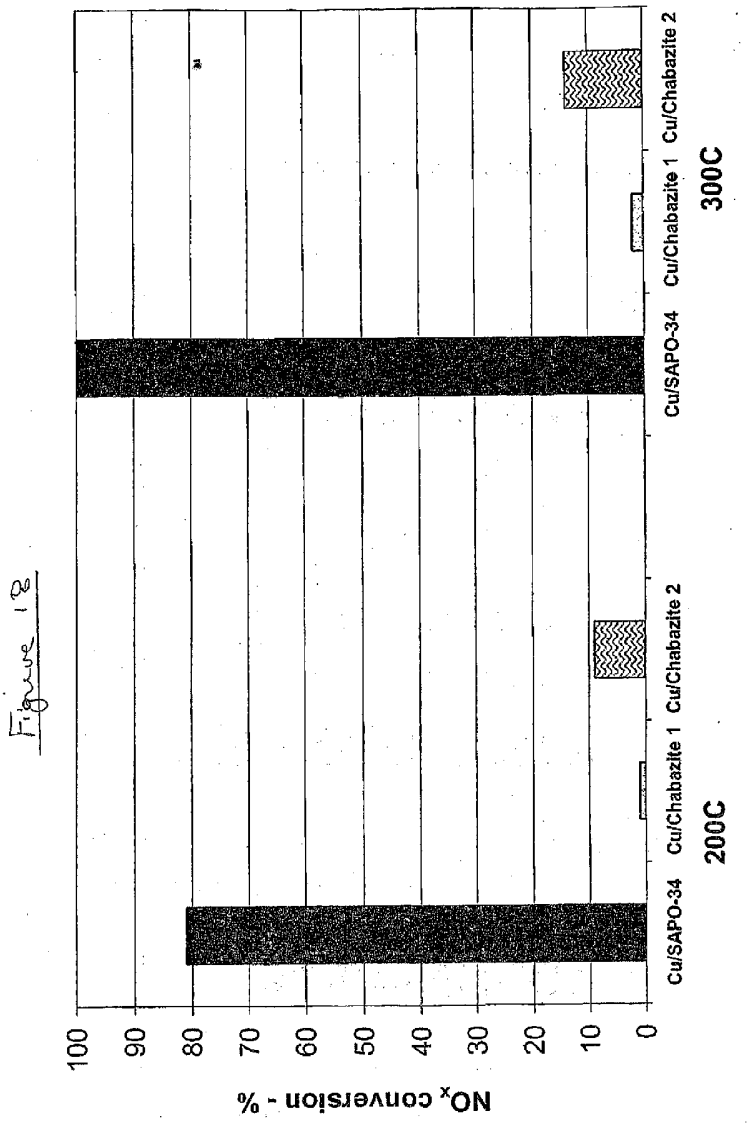
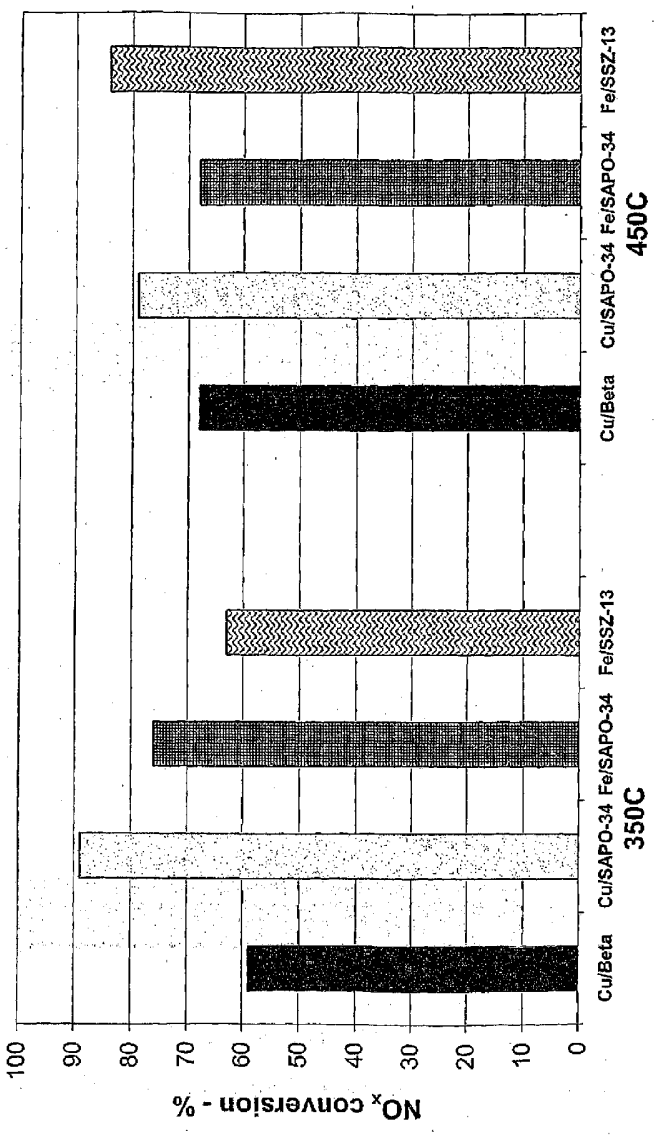

NOx conversion - %
100
90
80
70
60
50
40
30
20
10
0
Cu/SAPO-34
Cu/Chabazite 1
Cu/Chabazite 2
200C
Cu/SAPO-34
Cu/Chabazite 1
Cu/Chabazite 2
300C

Figure 18

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

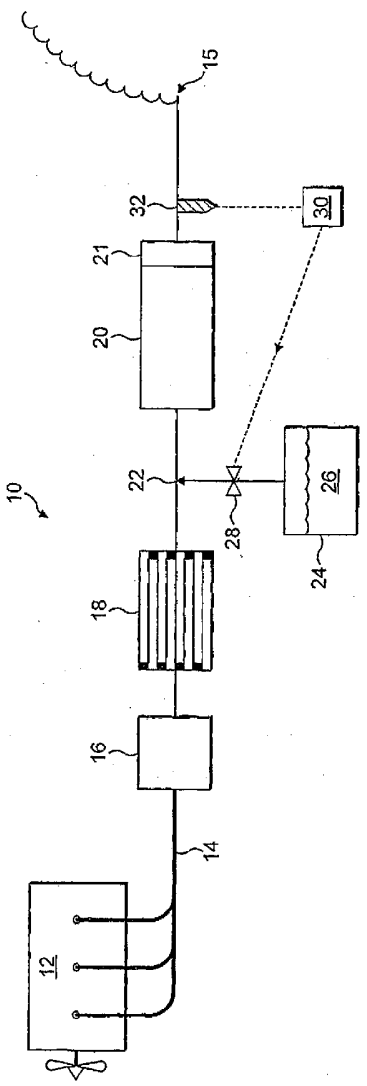


FIG. 20