



## Deactivation-resistant catalyst for selective catalyst reduction of NOx

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*Publication date:*  
2011

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Jensen, A. D., Castellino, F., Rams, P. D., Pedersen, J. B., & Putluru, S. S. R. (2011). Deactivation-resistant catalyst for selective catalyst reduction of NOx. (Patent No. *WO 2011073396*).

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(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
23 June 2011 (23.06.2011)

(10) International Publication Number  
**WO 2011/073396 A2**

(51) International Patent Classification:

*B01J 21/06* (2006.01)      *B01J 37/02* (2006.01)  
*B01J 21/10* (2006.01)      *B01D 53/00* (2006.01)  
*B01J 23/28* (2006.01)      *B01J 20/00* (2006.01)  
*B01J 23/30* (2006.01)

(21) International Application Number:

PCT/EP2010/070087

(22) International Filing Date:

17 December 2010 (17.12.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

09179933.8 18 December 2009 (18.12.2009) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH,

[Continued on next page]

(54) Title: DEACTIVATION-RESISTANT CATALYST FOR SELECTIVE CATALYST REDUCTION OF NO<sub>x</sub>

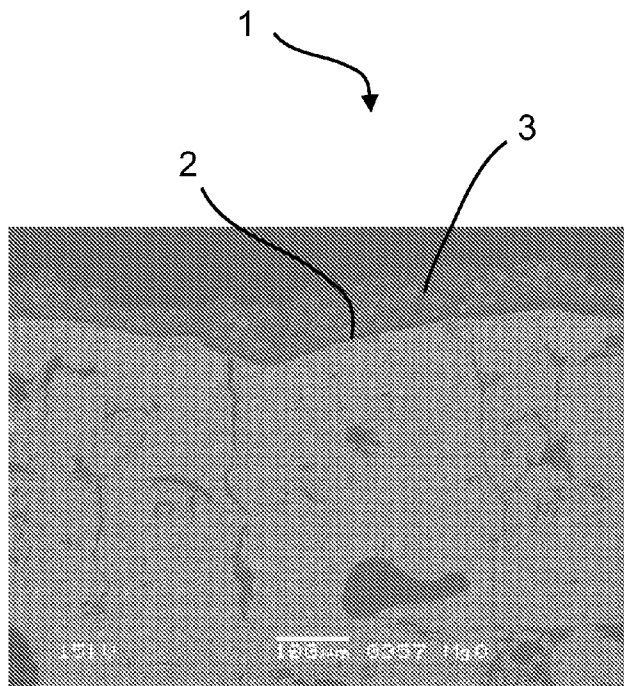


Fig. 1A

(57) Abstract: The present invention relates to a catalyst for selective catalytic reduction of NO<sub>x</sub> in alkali metal containing flue gas using ammonia as reductant, the catalyst comprising a surface with catalytically active sites, wherein the surface is at least partly coated with a coating comprising at least one metal oxide. In another aspect the present invention relates to the use of said catalyst and to a method of producing said catalyst. In addition, the present invention relates to a method of treating an catalyst for conferring thereon an improved resistance to alkali poisoning.



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GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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- *of inventorship (Rule 4.17(iv))*

**Published:**

- *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

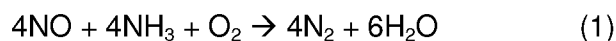
**Declarations under Rule 4.17:**

Deactivation-resistant catalyst for selective catalytic reduction of NO<sub>x</sub>

The present invention relates to a novel catalyst for selective catalytic reduction of NO<sub>x</sub> in alkali metal containing flue gas, to the use thereof, and to a method of producing  
5 said catalyst. In addition, the present invention relates to a method of treating an catalyst for conferring thereon an improved resistance to alkali poisoning.

Energy production by firing of organic material such as coal, oil, gas or biomass usually results in the production of undesired air pollutants such as NO<sub>x</sub> (NO and NO<sub>2</sub>). These  
10 are emitted into the environment as part of the resulting flue/exhaust streams. Combustion-derived NO<sub>x</sub> contributes to ground-level ozone formation, photochemical smog and acid rain, thereby deteriorating soils and damaging forests. NO<sub>x</sub> also constitutes a direct health concern as it may impact the human immune system, e.g. through formation of toxic organic nitrates. NO<sub>2</sub> reacts in the air to form nitric acid which  
15 is highly corrosive to building materials. In addition, NO<sub>x</sub> is believed to contribute to the depletion of stratospheric ozone. Consequently, the emission of NO<sub>x</sub> into the atmosphere is subject to stringent government regulations.

Selective catalytic reduction (SCR) by ammonia (NH<sub>3</sub>) is a widely used industrial  
20 process for reducing NO<sub>x</sub> emission from flue gas of stationary power units. In SCR, NO<sub>x</sub> is catalytically reduced to N<sub>2</sub> in the presence of oxygen with ammonia being added as the reducing agent. The injected ammonia reacts selectively with NO<sub>x</sub> at temperatures above about 230 °C in the presence of oxygen. The removal efficiency of SCR of NO<sub>x</sub> may be about 70-98%. For the reduction of NO, the following general  
25 stoichiometry applies:



Mechanistically, the SCR reaction with NO<sub>x</sub> and NH<sub>3</sub> is usually regarded as a process  
30 where ammonia adsorbs onto the catalyst surface whereupon NO reacts from the gas phase or as weakly adsorbed species.

In known SCR systems, there are three general classes of catalysts: precious-metal catalysts for operation at low temperatures, base metals for operation at medium  
35 temperatures, and zeolites for operation at higher temperatures. Base metal catalysts are often based on vanadium, for example as vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>), which may

be supported on titanium dioxide,  $\text{TiO}_2$ , and promoted with tungsten or molybdenum oxides. Examples of SCR catalyst compositions for  $\text{NO}_x$  reduction are  $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2$  or  $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ . For SCR with base metal catalysts, the most efficient reduction of  $\text{NO}_x$  is usually observed at operation temperatures of 300 - 450 °C. The choice of a suitable SCR catalyst for  $\text{NO}_x$  conversion typically depends on the temperature of the exhaust gas to be treated. It also usually depends on the amount of  $\text{SO}_2$  and  $\text{SO}_3$  present in the flue gas. Vanadium-based catalysts can in fact oxidise  $\text{SO}_2$  to  $\text{SO}_3$ . This latter can react with  $\text{NH}_3$  to form ammonium bisulfate, which may cause fouling and plugging of the catalyst.

10

A significant problem with SCR is catalyst deactivation caused by alkali metals such as potassium (K) or sodium (Na) that are present, for example, in flyash. Catalyst deactivation by chemical poisoning becomes manifest in decreased catalytic activity and selectivity. A highly undesired result of decreased catalytic activity is the release of excess  $\text{NH}_3$  from the SCR reactor. Excess  $\text{NH}_3$  can result in formation of ammonium bisulfate which may cause fouling of downstream equipment.

15

Deactivation by alkali metals is in particular observed when treating flue gas stemming from the firing of biomass. The latter is becoming increasingly popular in view of its even  $\text{CO}_2$  balance. A high level of alkali metals is typically also observed in waste incineration plants. In the combustion of biomass, alkali metals are usually present as aerosols. The deactivation of the catalyst is believed to be mainly caused by potassium nanoparticles. These particles are produced during the combustion of biomass by the decomposition and subsequent condensation of potassium compounds at high temperatures.

25

Biomass such as straw or woodchips may contain up to 2 wt% potassium and may result in a high content of flyash. The potassium content in such flyash may be up to 40 wt%. Both factors contribute to an increased deactivation of SCR catalysts when treating flue gas from burned biomass. For purely biofired units, alkali metal poisoning has so far been an obstacle for SCR installation in the high-dust position, which is an SCR configuration that has the advantage of not requiring particulate emissions control prior to the  $\text{NO}_x$  reduction process.

30

Catalyst poisoning by alkali metals and alkaline earth metals usually depends on the basicity of the metal, which leads to the following sequence of deactivation potential K

35

> Na > Ca. Hence, deactivation is proportional to the basicity, which makes potassium particles, such as potassium oxides, the main culprit. Cs and Rb have an even higher deactivation potential, however, these metals do not usually occur in substantial amounts in firing materials.

5

Deactivation by potassium relates to the loss of Brønsted acid sites (V-OH groups) and to the decreased activity of the Lewis acid sites (V=O groups) of vanadium oxide based SCR catalysts. Alkali metals bind to the ammonia adsorption sites resulting in a permanent deactivation of the catalyst. The poisoning mechanism is believed to be a reaction of the V-OH groups with a potassium compound, such as  $K_2O$  where the hydrogen atom is replaced by potassium. Subsequently, potassium atoms may diffuse into the catalyst to bind to new Brønsted acid sites whereby the initial site may be attacked by another potassium atom. Similarly, potassium cations may associate with several Lewis acid sites on the catalytic surface. Overall, the deactivation mechanism is believed to include the steps of (i) deposition of alkali-containing flyash on the catalyst surface, (ii) reaction between the alkali metal and the catalytic surface resulting in bonding of alkali metal to the catalyst surface, and (iii) diffusion of alkali metal atoms into the catalyst following the concentration gradient.

20 Another aspect of alkali metal poisoning is the typically observed shift of the maximum catalytic activity towards lower temperatures, which complicates the overall operation procedure of SCR systems treating biomass exhaust gas.

Known attempts at minimising alkali metal deactivation of SCR catalysts include the addition of  $SO_2$  to the flue gas stream. The acidity of the injected  $SO_2$  is believed to regenerate Brønsted acid sites. Also, it has been suggested to use alternative support materials other than  $TiO_2$ , such as  $Zr(SO_4)_2$  or sulphated zirconium dioxide ( $ZrO_2$ ) with either sulphate or tungsten as an additive. These approaches focus on enhancing the acidity of the catalyst and/or its carrier, which thus appears to be a prejudice in the art.

30

It has also been proposed to increase the number of catalytically active vanadium sites in order to decrease the relative influence of the deposited alkali metals. In view of the comparatively high price of vanadium, this strategy is not very cost-efficient. Furthermore, the addition of vanadium results in an increased activity only when a monolayer of vanadium oxide is formed on the support, meaning that the available surface area of the support is limiting this practice.

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International Patent Application No. WO/2008/037255 relates to the selective removal of NO<sub>x</sub> from flue gas originating from the burning of biomass, combined biomass and fossil fuel, and from waste incineration units, i.e. gases containing a significant amount of alkali metal and/or alkali-earth compounds. The proposed SCR catalyst comprises a formed porous superacidic support, a metal oxide catalytic component selected from the group consisting of Cu, V, Fe, Cr, Mn, and any mixtures thereof, deposited on said support. The superacidic support is produced by depositing acid sulphates such as sulphuric acid onto ZrO<sub>2</sub>, SnO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub>. This is time-consuming and can hardly be applied to existing catalysts, where the support is already covered with the catalytic components.

European Patent Application EP 1 358 933 A1 relates to a catalyst used for exhaust gas purification and NO<sub>x</sub> removal for an internal combustion engine. The catalytically active components may comprise alkaline metals or alkaline-earth metals such as sodium potassium, lithium, cesium, strontium or barium, in the form of oxides together with at least one noble metal or rare earth metal. To suppress sintering and migration of the metals outside the carrier and into the substrate, the catalysts comprise an anchoring material, which preferably is MgO. The catalyst is thus made up of a substrate, which is coated with a carrier containing an anchoring material such as MgO, which subsequently is impregnated with the catalytically active component.

United States Patent US 3,990,998 A relates to a ruthenium catalyst system for treatment of waste gases and NO<sub>x</sub> removal. The problem addressed by US 3,990,998 A is the prevention of ruthenium oxide formation at high temperatures. The solution is a system where a core is coated first with Al<sub>2</sub>O<sub>3</sub>, then with MgO, and finally with catalytic quantities of Ru. Similar to EP 1 358 933 A, US 3,990,998 teaches the application of MgO onto or into the carrier system followed by coating/impregnating with the catalytically active components.

United States Patent Application US 2009/253941 A1 discloses a microchannel device with a supported formaldehyde synthesis catalyst for converting methanol to formaldehyde. The catalyst may be produced by impregnating a MoO<sub>3</sub>/TiO<sub>2</sub> powder with a vanadium-containing aqueous solution, followed by calcination. Subsequently, iron is added by ion exchange using a FeCl<sub>2</sub> solution, resulting in a final Fe<sub>2</sub>O<sub>3</sub> content of 2%.

Consequently, it is a first object of the present invention to provide a catalyst with an improved resistance to alkali poisoning during selective catalytic reduction of NO<sub>x</sub> using ammonia as the reductant.

It is a second object of the present invention to provide a catalyst with an increased catalyst lifetime for selective catalytic reduction of NO<sub>x</sub> using ammonia as the reductant.

It is a third object of the present invention to provide a cost-effective and easily manufacturable catalyst for selective catalytic reduction of NO<sub>x</sub> using ammonia as the reductant.

It is a fourth object of the present invention to provide a catalyst for selective catalytic reduction of NO<sub>x</sub> using ammonia as the reductant, said catalyst being resistant to alkali poisoning without the need of injecting further reactants to the flue gas.

It is a fifth object of the present invention to provide a catalyst suitable for SCR installation in the high-dust position on biofired power units.

It is a sixth object of the present invention to provide a method for treating existent SCR catalysts for conferring thereon an improved resistance to alkali poisoning during selective catalytic reduction of NO<sub>x</sub> using ammonia as the reductant.

The new and unique way of addressing one or more of the above-mentioned objects is to provide a catalyst for selective catalytic reduction of NO<sub>x</sub> in alkali metal containing flue gas using ammonia as reductant, the catalyst comprising a surface with catalytically active sites, wherein the surface is at least partly coated with a coating comprising at least one metal oxide.

In another aspect, the present invention relates to a use of the inventive catalyst for selectively reducing NO<sub>x</sub> in alkali metal containing flue gas using ammonia as reductant.

35



It is another aspect of the present invention to provide a method of producing a catalyst according to the present invention, the method comprising providing a support, impregnating the support with a first aqueous solution comprising a vanadium component, drying and calcining the impregnated support, coating the impregnated support with a second aqueous suspension comprising at least one metal oxide, drying and calcining the coated support for a second time.

Yet another aspect of the present invention is a method of treating an uncoated catalyst for conferring thereon an improved resistance to alkali poisoning during selective catalytic reduction of  $\text{NO}_x$  using ammonia as the reductant, the catalyst comprising a surface with catalytically active sites, the method comprising coating the surface at least partly with a coating comprising at least one metal oxide.

As used herein, the term "vanadium-based catalyst" refers to a catalyst that comprises one or more vanadium containing compounds, such as vanadium oxides, as catalytic components for ammonia adsorption and  $\text{NO}_x$  reduction. A preferred example is  $\text{V}_2\text{O}_5$ .

As used herein, the term "basic metal oxides" refers to metal oxides that form hydroxides or dissolve by forming basic aqueous solutions when reacting with water. Examples of basic metal oxides include  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{BaO}$ ,  $\text{SrO}$  or lanthanide oxides. Of the divalent oxides, it is found that basicity increases as expected in the order  $\text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$ . An example of an oxide not falling within this definition of "basic metal oxides" is  $\text{V}_2\text{O}_5$ , which is an acid oxide.

As used herein, the term "catalytically active sites" refers to the Brønsted (proton donor) and Lewis (electron acceptor) acid sites on the catalyst for adsorption of ammonia. For catalysts comprising  $\text{V}_2\text{O}_5$ , the Brønsted acid sites correspond to V-OH groups and the Lewis acid sites correspond to  $\text{V}=\text{O}$ .

As used herein, the term "fully coated" refers to a situation where at least 98% of the catalyst surface with catalytically active sites (e.g. V-OH or  $\text{V}=\text{O}$ ) is coated with a coating comprising one or more metal oxides.

As used herein, the term "uncoated catalyst" refers to a catalyst where the surface containing the catalytically active sites (for example V-OH and/or  $\text{V}=\text{O}$ ) is uncoated and thereby directly exposed to the surroundings.

Figure 1 shows two scanning electron microscopy (SEM) images of a cross section of a coated catalyst according to the present invention. The SEM images were taken by using a thin carbon coating. The left image (Fig. 1A) represents a magnification of x150, while the right image (Fig. 1B) represents a magnification of x1000.

Figure 2 shows an SEM image of a cross section of a non-coated catalyst (comparative) after exposure to KCl nanoparticles (Fig. 2A). Ten points along the cross section were analysed with EDX resulting in the potassium concentrations (in wt%) shown in Fig. 2B (the abscissa represents weight percentages of potassium, while the ordinate represents the distance in  $\mu\text{m}$ ).

Figure 3 shows an SEM image of a cross section of a coated catalyst according to the present invention after exposure to KCl nanoparticles (Fig. 3A). Ten points along the cross section were analysed with EDX resulting in the potassium concentrations (in wt%) shown in Fig. 3B (the abscissa represents weight percentages of potassium, while the ordinate represents the distance in  $\mu\text{m}$ ).

In a first aspect, the present invention relates to a catalyst for selective catalytic reduction of  $\text{NO}_x$  in alkali metal containing flue gas using ammonia as reductant, the catalyst comprising a surface with catalytically active sites, wherein the surface is at least partly coated with a coating comprising at least one metal oxide.

Since the surface with catalytically active sites (for example V-OH and/or V=O) is partly or fully coated with the coating comprising at least one metal oxide, it is evident that the coated part of the surface with the catalytically active sites is no longer directly exposed to the surroundings, i.e. is no longer a free surface. The actual free face of a fully coated catalyst according to the present invention would then obviously be constituted by the outer side of the coating.

The inventive catalyst leads to surprisingly slow rates of alkali deactivation even at full biomass firing. As described above, the alkali poisoning mechanism for known vanadium-based SCR catalysts is believed to involve an acid-base interaction between the catalytic surface (acid) and alkali metals such as potassium (base). The catalyst according to the present invention thus provides a coating comprising metal oxides which is believed to (i) exhibit a lower degree of reaction with alkali metals derived from

flyash and to (ii) prevent migration of alkali metals to the active sites of the catalyst. Without wishing to be bound by theory, it is believed that the degree of the acid-base reaction is the decisive parameter for deactivation. Preventing this reaction from taking place by using metal oxides presents a breakthrough in producing alkali-poisoning resistant SCR catalysts. It is believed that potassium atoms are stable in the flyash particle or form a K-O complex at the surface of the metal oxide layer, which substantially leads to immobilization of potassium.

Again without wishing to be bound by theory it is believed that an additional effect may contribute to achieving the surprisingly slow rates of alkali deactivation of the present catalyst. Some of the metal of the metal oxide, for example Mg, may migrate into and beyond the surface with the catalytically active sites. The Mg thus present on the catalytically active sites constitutes a relatively weak catalyst poison that may effectively block alkali metals such as potassium from adhering to the same.

The coating should be thin enough to allow cross-layer diffusion of  $\text{NH}_3$  and  $\text{NO}_x$  towards the active sites of the catalyst. While potassium is substantially prevented from crossing the coating layer,  $\text{NH}_3$  and  $\text{NO}_x$  advantageously travel across the coating to the catalytically active sites where the actual reduction of  $\text{NO}_x$  takes place.

The layer may cover the surface with the catalytically active sites fully or partly. The latter may be useful when a catalyst with a high initial activity together with a satisfactory long term resistance to alkali poisoning is required. Since the coating may reduce the activity of the catalyst to some degree, as compared to an uncoated reference catalyst, it may be desired to keep part of the surface area uncoated. However, even a fully coated catalyst has surprisingly been found to exhibit only a minor reduction in activity, which is a reasonable trade-off in view of the improved deactivation resistance. This is particularly surprising in view of the above-discussed prior art teaching that the catalytically active components are to be applied onto a carrier system comprising MgO. By reversing this order in accordance with the present invention a completely counterintuitive effect is achieved in that a considerably higher activity is maintained over a longer time period.

The inventive catalyst may be a monolithic catalyst. The catalyst may be of the extruded honeycomb type, the plate catalyst type, or the corrugated plate catalyst type.

According to a preferred embodiment of the present invention, the catalyst is a vanadium-based catalyst.

5 According to a preferred embodiment of the present invention, the metal oxide is a basic metal oxide. As described above, the prior art suggests that acid support materials such as superacidic  $ZrO_2$  lead to a better resistance against alkali metal poisoning of the catalyst. However, it has now surprisingly been observed that in particular a basic metal oxide coating confers an improved resistance to alkali poisoning on the catalyst. For known uncoated catalysts, the poisoning reaction is  
10 essentially an acid-base interaction, where the catalytic surface represents the acid and the alkali metal represents the base. By providing the catalyst with a basic metal oxide layer this type of interaction is believed to be minimal, resulting in an improved resistance to deactivation by alkali metals.

15 According to a particularly preferred embodiment of the present invention, the metal oxide is MgO. MgO is highly refractory and non-toxic. In addition, MgO is cheap and readily available in large quantities. Furthermore, MgO exhibits advantageous properties with respect to porosity and gas permeability of the coating. MgO layers were observed to readily permit cross-layer transport of  $NO_x$  and  $NH_3$  while at the same  
20 time efficiently retaining alkali atoms.

According to another embodiment of the present invention, the surface is fully coated with the coating. The advantage of this is a complete protection of the catalytically active sites which gives a better long-term resistance to alkali poisoning as compared  
25 to a catalyst with a partly coated surface.

According to another embodiment of the present invention, the coating further comprises one or more coating additives. Thereby, the adherence of the coating to the surface containing the catalytically active sites may be improved. Possible additives  
30 include oxides of titanium, chromium and manganese. Other possible additives include boron, clay minerals, feldspar or ZnO. These may reduce crazing of, for example, MgO coatings.

According to a preferred embodiment of the present invention, the coating additive  
35 comprises one or more boron compounds. The boron compound may, for example, be boric acid or a boron oxide such as boric anhydride ( $B_2O_3$ ). Boron compounds are

believed to minimise crazing of the catalyst coating. Boron compounds are also believed to improve the conditions of sintering providing a liquid phase at the grain boundaries and improving chemical bonding. Boron may be present in the coating at a concentration of 1-5 wt%.

5

According to another embodiment of the present invention, the coating has a thickness of 1-100  $\mu\text{m}$ . This range of coating thickness is believed to present a satisfactorily thin diffusion barrier for gaseous  $\text{NO}_x$  and  $\text{NH}_3$ , while being able to retain potassium lest it reach the catalytically active sites. It was surprisingly observed that the coated catalyst with this thickness range may retain up to 80% of its original, non-coated activity. Even more preferably the coating has a thickness of 30-70  $\mu\text{m}$ .

According to another embodiment of the present invention, the catalyst comprises either (i)  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  on  $\text{TiO}_2$  or (ii)  $\text{V}_2\text{O}_5$  and  $\text{WO}_3$  on  $\text{TiO}_2$ . A useful composition for the present invention is 5 wt%  $\text{V}_2\text{O}_5$ , 9 wt%  $\text{WO}_3$  and the remainder  $\text{TiO}_2$  (anatase) reinforced with fibre material. Another example is the vanadium-based catalyst DNX-964 available from Haldor Topsoe A/S.

The inventive catalyst may be advantageously incorporated into an SCR reactor. The reactor may be of the monolith reactor type, the parallel plate type or the lateral flow reactor type.

In another embodiment of the present invention, the catalyst comprises zeolites of structure type BEA, MFI loaded with metal, preferentially Fe and Cu.

25

The present invention also relates to a use of the inventive catalyst for selectively reducing  $\text{NO}_x$  in alkali metal containing flue gas using ammonia as reductant. The inventive catalyst may be used in stationary or mobile SCR applications, such as power plants, heat recovery steam generators, waste heat boilers, process heaters or gas turbines.

According to a preferred embodiment of the present invention, the flue gas originates from the firing of biomass. Biomass may include tree and grass crops, wood, waste material from agriculture, forestry or industry, or urban wastes. The firing of biomass may also include co-firing of biomass and, for example, coal.

35

The present invention also relates to a method of producing the inventive catalyst, the method comprising providing a support, impregnating the support with a first aqueous solution comprising a vanadium component, drying and calcining the impregnated support, coating the impregnated support with a second aqueous suspension  
5 comprising at least one metal oxide, and drying and calcining the coated support for a second time. In the first step, the support is preferably homogeneously impregnated with, for example, vanadium pentoxide and tungsten trioxide. Here, the incipient wetness method may be used. In the second step, i.e. the coating, different techniques may be used such as sol-gel, wash-coating, vacuum coating or electrostatic spray  
10 deposition. The coating step may also be carried out by sintering. The subsequent calcination step is useful for improving the attachment of the coating to the catalyst surface.

According to a preferred embodiment of the method according to the present invention,  
15 the metal oxide is a basic metal oxide.

According to a particularly preferred embodiment of the method according to the present invention, the metal oxide is MgO.

20 According to an expedient embodiment, the coating of the support with the second aqueous suspension is carried out by a spraying method selected from air-atomized spraying, air-assisted spraying, airless spraying, high volume low pressure spraying, and air-assisted airless spraying. Coating by a spraying method, for example air atomized spraying using a spray gun, resulted in a particularly thin coating layer while  
25 the original surface structure of the catalyst could still be observed. The thin coating layer, which is preferably between 1-100  $\mu\text{m}$ , allows for an efficient transport of gaseous  $\text{NO}_x$  and  $\text{NH}_3$  across the coating.

Alternatively, the coating of the support with the second aqueous suspension is carried  
30 out by a wash-coating method.

Another aspect of the present invention is a method of treating an uncoated catalyst for conferring thereon an improved resistance to alkali poisoning during selective catalytic reduction of  $\text{NO}_x$  using ammonia as the reductant, the catalyst comprising a surface  
35 with catalytically active sites, the method comprising coating the surface at least partly with a coating comprising at least one metal oxide. Thereby, existing prior art catalysts

can be upgraded in terms of resistance to alkali poisoning. This is cost-efficient and environmentally friendly as compared to producing new catalysts from scratch.

According to a preferred embodiment of the inventive method, the metal oxide is a  
5 basic metal oxide.

According to a particularly preferred embodiment of the inventive method, the metal oxide is MgO.

10 According to a preferred embodiment of the inventive method, the uncoated catalyst is a vanadium-based catalyst.

The uncoated catalyst may comprise zeolites.

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#### Example 1: Catalyst coating

1.7 x 1.7 cm<sup>2</sup> (0.3 g) catalyst plates from Haldor Topsøe A/S were used. The composition of the catalyst was 1.2 wt% V<sub>2</sub>O<sub>5</sub>, 7 wt% WO<sub>3</sub> and TiO<sub>2</sub> (anatase)  
20 reinforced with fibre material. The fibre material mainly consisted of SiO<sub>2</sub> with alumina and calcium as minor components. The catalyst plates were coated with an aqueous MgO suspension containing 15-30 mass percent dry matter. The coating was applied with a spray gun at 1.5 bar and a nozzle diameter of 0.5 mm, the nozzle held at a distance of 30-35 cm from the catalyst plate. The average particle diameter in the  
25 applied MgO suspension was about 22 µm. Coated plates were subsequently calcinated for four hours at 500 °C. The average thickness of the MgO coating was 64 µm. An exemplary SEM image of the coated catalyst 1 is shown in Figs. 1A and 1B. Both magnifications in Fig. 1 show the surface 2 with catalytically active sites, which is coated with the MgO-coating 3.

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#### Example 2: Exposure to potassium nanoparticles

Both a coated catalyst and a non-coated reference catalyst were exposed to potassium nanoparticles at pilot plant scale. The pilot plant was operated at a burner temperature  
35 of 1100 °C. An aqueous potassium chloride (7.4 g/L) was injected into the burner over a period of 648 hours at a flow rate of about 400 mL/h. The tested catalysts were

exposed to the potassium containing exhaust stream at a temperature of 350 °C and a flow of 40 Nm<sup>3</sup>/h (Nm<sup>3</sup>/h is equal to m<sup>3</sup>/h at standard conditions). Thus, each catalyst was exposed to a KCl nanoparticle concentration of about 53 mg/Nm<sup>3</sup>.

#### 5 Example 3: Determination of catalytic activity

Catalytic activity was determined in a quartz reactor with the catalyst plates resting on a frit. The flow was held constant at 3 L/min with concentrations of about 370 ppm NO, 500 ppm NH<sub>3</sub>, 5 vol% O<sub>2</sub> and 1.4 vol% H<sub>2</sub>O. All measurements were conducted at a  
10 temperature of 350 °C. The rate constant for the reduction of NO with NH<sub>3</sub> was calculated via the measured consumption of NO. Catalytic activity was tested for three different types of plate: (i) non-coated catalyst plates (comparative), (ii) coated catalyst plates, and (iii) KCl-exposed coated catalyst plates. This way it was possible to evaluate the effect of the coating as such, the effect of the potassium exposure, and  
15 the overall effect (coating + KCl-exposure).

The coating with MgO, as described above, resulted in an average decrease of catalytic activity on the order of 20%. This loss is ascribed to the necessity of NO<sub>x</sub> and NH<sub>3</sub> to diffuse through the coating layer prior to reaction at the active sites of the  
20 catalyst. Thus, about 80% of the original activity was maintained for the coated catalyst before exposure to KCl. After exposure to KCl-nanoparticles (see above) the catalytic activity of the coated catalyst according to the present invention was reduced by about 25% relative to the activity of the coated, non-exposed catalyst. However, the KCl-exposed, non-coated catalyst (comparative) exhibited a decrease in catalytic activity of  
25 about 75% relative to the non-exposed, non-coated reference (comparative). With regard to the combined effect of the coating and the KCl-exposure it was found that the inventive catalyst retained about 60% of its initial activity whereas the non-coated reference catalyst (comparative) retained only about 25% of its initial activity after KCl-exposure. This clearly demonstrates the superior properties of the coated catalyst  
30 according to the present invention with respect to resistance to potassium poisoning.

#### Example 4: Elemental analysis

Energy dispersive X-ray (EDX) analysis was used for investigating the elemental  
35 composition of a cross section of a MgO-coated catalyst according to the present invention as well as of a non-coated reference catalyst. For this purpose, the catalysts



were epoxy impregnated under vacuum and subsequently polished with a Struer Rotoforce-4 polishing station (5 Newton). After KCl-exposure the non-coated reference catalyst (comparative) had a surface potassium concentration of 6-25 wt% whereas the MgO-coated catalyst according to the present invention had an average surface potassium concentration of 19-26% (the term "surface" relates here to the surface of the coating).

A cross-sectional concentration profile of potassium after KCl exposure is shown in Fig. 2B for the non-coated reference catalyst (comparative). A steep concentration gradient of potassium can be observed on both sides of the catalyst plate with high potassium levels at the catalyst surface which rapidly drop at a depth of 100  $\mu\text{m}$  and deeper. The same analysis was done for the MgO-coated catalyst according to the present invention. A cross-sectional profile of the catalyst plate (excluding the coating) was analysed for potassium (Fig. 3B). The profile is essentially constant with depth. All measure potassium concentrations were below the measurement background noise, indicating that it is safe to assume that potassium is substantially absent. This finding demonstrates that potassium does not reach the actual catalyst due to the inventive coating.

Potassium levels in the coating were analyzed for areas 11 and 12 in Fig. 3A. The measured potassium levels on and within the coating were around 5 wt%. Apparently, the coating efficiently retains potassium atoms. A concentration profile across the inventive coating showed a substantially linear decrease of potassium levels from the surface of the coating to the coating/catalyst interface (not shown).

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It is evident that the details mentioned in the foregoing examples are illustrative and should not be construed as limiting the invention hereto.

Claims

1. A catalyst (1) for selective catalytic reduction of  $\text{NO}_x$  in alkali metal containing flue gas using ammonia as reductant, the catalyst (1) comprising a surface (2) with catalytically active sites, characterised in that the surface (2) is at least partly coated with a coating (3) comprising at least one metal oxide.  
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2. A catalyst according to claim 1, characterised in that the metal oxide is a basic metal oxide.  
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3. A catalyst according to claims 1 or 2, characterised in that the metal oxide is  $\text{MgO}$ .
4. A catalyst according to any one of the preceding claims, characterised in that the surface (2) is fully coated with the coating (3).  
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5. A catalyst according to any one of the preceding claims, characterised in that the coating (3) has a thickness of 1-100  $\mu\text{m}$ .
6. A catalyst according to any one of the preceding claims, characterised in that the catalyst comprises either (i)  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  on  $\text{TiO}_2$  or (ii)  $\text{V}_2\text{O}_5$  and  $\text{WO}_3$  on  $\text{TiO}_2$ .  
20
7. A catalyst according to any one of the preceding claims, characterised in that the catalyst comprises zeolites of structure type BEA, MFI loaded with metal, preferentially Fe and Cu.  
25
8. Use of a catalyst according any one of claims 1-7 for selectively reducing  $\text{NO}_x$  in alkali metal containing flue gas using ammonia as reductant.
9. Use according to claim 8, where the flue gas originates from the firing of biomass.  
30
10. Method of producing a catalyst according to any one of claims 1-7, the method comprising providing a support, impregnating the support with a first aqueous solution comprising a vanadium component, drying and calcining the impregnated support, coating the impregnated support with a second aqueous suspension comprising at least one metal oxide, and drying and calcining the coated support for a second time.  
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11. Method according to claim 10, wherein the metal oxide is a basic metal oxide.
12. Method according to claim 11, wherein the metal oxide is MgO.
- 5 13. Method according to any one of claims 10-12, wherein the coating of the support with the second aqueous suspension is carried out by a spraying method selected from air-atomized spraying, air-assisted spraying, airless spraying, high volume low pressure spraying, and air-assisted airless spraying.
- 10 14. Method according to any one of claims 10-12, wherein the coating of the support with the second aqueous suspension is carried out by a wash-coating method.
- 15 15. Method of treating an uncoated catalyst for conferring thereon an improved resistance to alkali poisoning during selective catalytic reduction of NO<sub>x</sub> using ammonia as the reductant, the catalyst comprising a surface with catalytically active sites, the method comprising coating the surface at least partly with a coating comprising at least one metal oxide.
- 20 16. Method according to claim 15, wherein the metal oxide is a basic metal oxide.
17. A method according to claim 16, wherein the metal oxide is MgO.

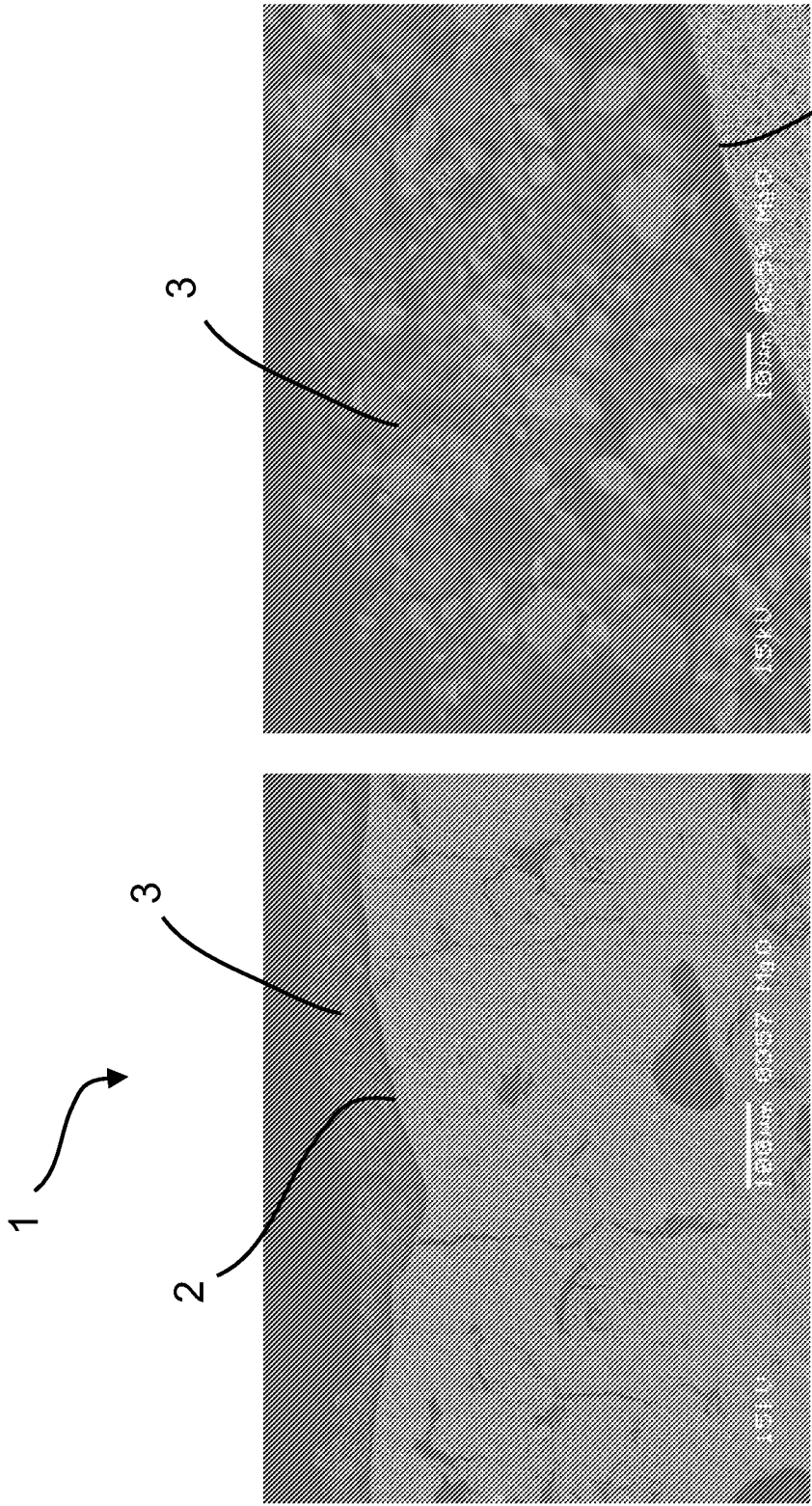


Fig. 1B

Fig. 1A

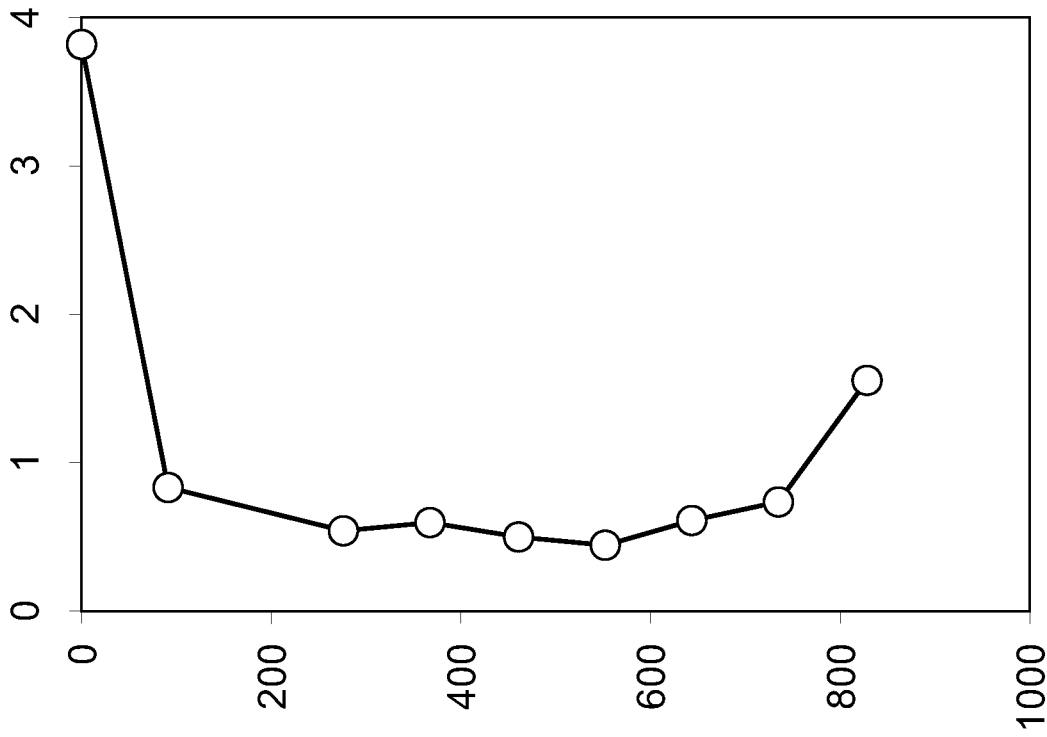


Fig. 2B

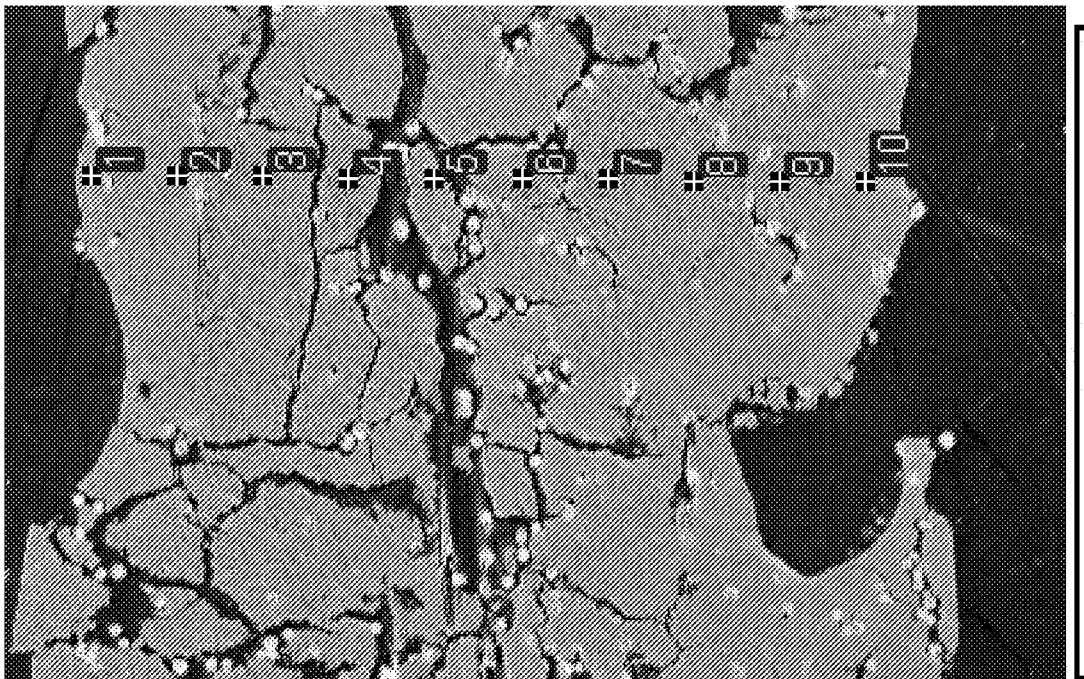


Fig. 2A

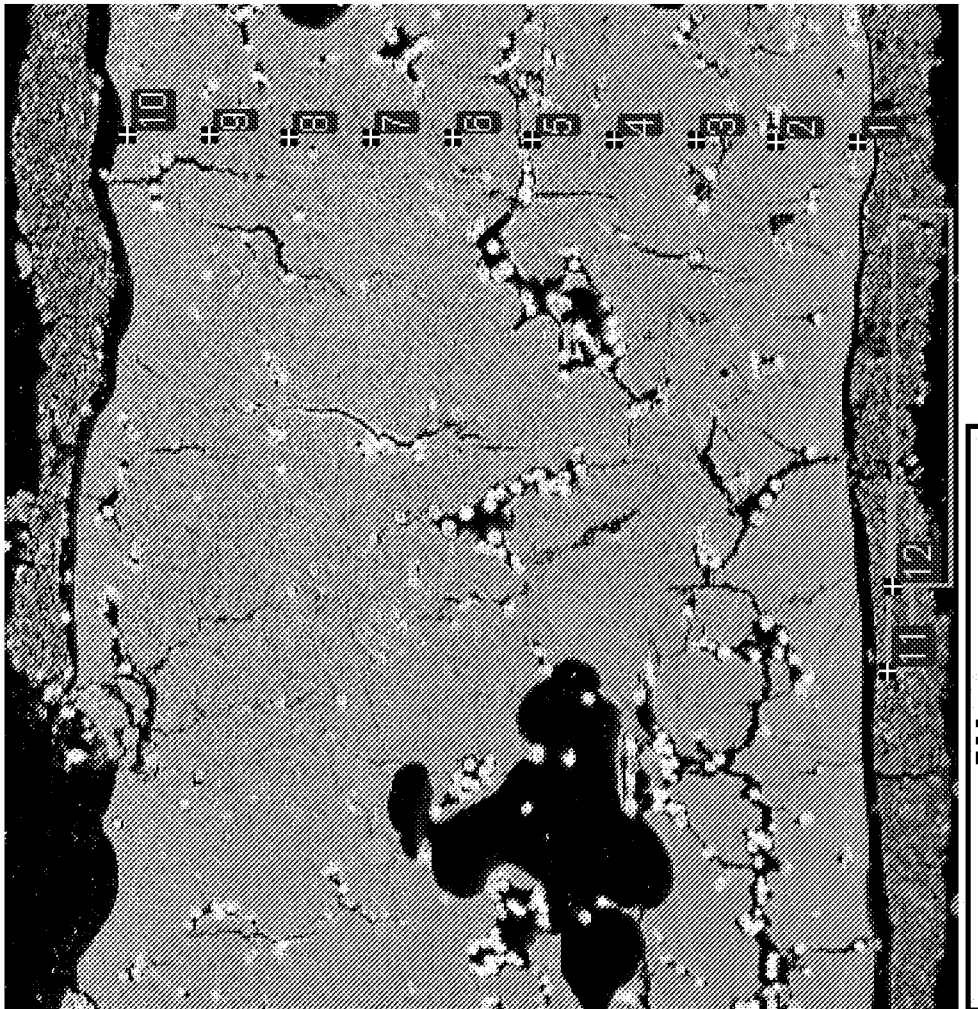


Fig. 3A

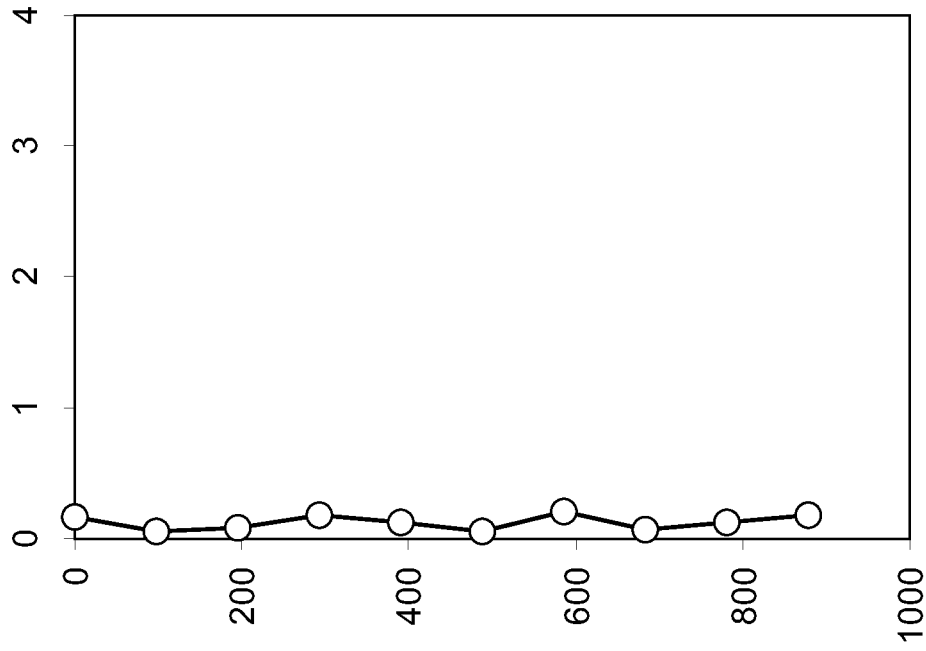


Fig. 3B