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GB-A- 2 096 482
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US-A- 4 912 072
US-A1- 2006 211 569
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Description

The present invention relates to a process in particular for the production of a precursor of a supported platinum catalyst.

Supported noble metal catalysts, in which comparatively small noble metal particles are deposited on the surface of a solid support, are used in particular in synthetic chemical and petrochemical processes for converting a wide variety of starting materials into desired intermediates or end products or for chemically refining various fractions of petroleum processing. In addition, supported noble metal catalysts are used in particular also as oxidation catalysts in the purification of exhaust gases from combustion engines.

Supported catalysts loaded with noble metal are generally produced by means of a multi-stage process. In that process, for example, in a first step, a support material is impregnated with a noble metal salt solution of the desired noble metal. After removal of the solvent from the support material in a subsequent step, the support material is then calcined in a further step, wherein the noble metal can be converted into an oxide form by the heat treatment. Then, in a further step, the noble metal component is converted into the catalytically active, highly disperse noble metal in the oxidation state 0 by means of hydrogen, carbon monoxide or wet chemical reducing agents, for example. For storage purposes, the supported noble metal catalyst can be stabilized in a final step, for example by wet stabilization by means of an oil or by dry stabilization by means of partial oxidation (passivation) of the deposited noble metal particles.

The activity of supported noble metal catalysts is generally dependent on the size of the noble metal particles. The supported noble metal catalysts known in the prior art have the disadvantage that they lose activity as they are used owing to sintering of the noble metal particles to larger units and an associated reduction in catalytically active surface. The rate of this so-called thermal ageing process is dependent on the temperature at which the catalyst is used. In fact, the rate of the so-called ageing process increases as the use temperature increases, which is presumably caused by increased mobility of the noble metal particles on the support material surface and an associated increased sintering tendency.

US 4,912,072 discloses a zeolitic catalyst of the structure type L, which is produced by treatment of the zeolite powder with an aqueous $Pt(NH_3)_4Cl_2H_2O$ solution under sound and subsequent reduction with hydrogen. With a platinum content of less than 2×10^{-2} mmol Pt/g, only the inner surface is coated with platinum in the platinum catalyst so produced.

US 2006/0211569 A1 discloses an oxidation catalyst for the treatment of exhaust gases, which catalyst is produced by impregnating a washcoat consisting of a temperature-resistant inorganic oxide, a zeolite and tin oxide with platinum sulphite acid by the pore filling process, followed by drying and calcination.

A large number of attempts have already been made in the prior art to produce catalysts which are highly active in high-temperature applications and are subjected to only a slight thermal ageing process. Kubanek *et al.* "Microporous and Mesoporous Materials 77 (2005) 89-96", for example, describe the production of a supported platinum catalyst by impregnation of a zeolite of the structure type MFI (SH27) with the Pt precursor compound $Pt(NH_3)_4(NO_3)_2$ and subsequent calcination of the zeolite loaded with the precursor compound under a protective gas atmosphere. When using $Pt(NH_3)_4(NO_3)_2$, autoreduction occurs at relatively high temperatures. However, the supported platinum catalyst so produced has comparatively low activity and also a comparatively high tendency to thermal ageing.

Accordingly, the object of the present invention is to provide a process in particular for the production of a platinum catalyst precursor, by means of which supported platinum catalysts can be produced which have increased activity compared with the platinum catalysts known from the prior art.

It is a further object of the present invention to provide a process for the production of a platinum catalyst precursor, by means of which supported platinum catalysts can be produced which have a comparatively low tendency to thermal ageing and accordingly retain their catalytic activity substantially unchanged over long service lives.

The object is achieved by a process comprising the steps:

a) impregnation of an open-pored support material with platinum sulphite acid;

b) calcination of the impregnated support material under a protective gas.

Surprisingly, it has been found that by means of the process according to the invention there is obtainable a platinum catalyst precursor from which there results, after conversion of the platinum component into the oxidation state 0, a supported platinum catalyst which is distinguished by increased activity.

In addition, it has been found, surprisingly, that by impregnation of an open-pored support material with platinum sulphite acid and calcination of the impregnated support material under a protective gas atmosphere there is obtainable a platinum catalyst precursor by means of which, by reduction of the platinum component into the oxidation state 0, a supported platinum catalyst can be produced which, at comparatively high temperatures, has a very low tendency to thermal ageing and retains its catalytic activity largely unchanged over comparatively long service lives.

These advantages of a platinum catalyst produced by the route of the process according to the invention come to bear in particular in high-temperature applications, such as, for example, in oxidation catalysis, in which corresponding platinum catalysts produced by conventional routes have a tendency to rapid thermal ageing owing to a high mobility of the platinum particles, effected by the prevailing high temperatures, and an associated increased sintering tendency.

By means of the process according to the invention it is possible to produce platinum catalyst precursors and therefrom, after reduction, ultimately supported platinum catalysts, that is to say supported platinum catalysts which comprise Pt in the oxidation state 0. The platinum catalysts can be both metal catalysts which comprise, in addition to Pt in the oxidation state 0, one or more additional transition metals in any desired oxidation state or in the oxidation state 0, preferably noble metals, and pure platinum catalysts which contain only Pt in the oxidation state 0 as the catalytically active metal. If a further transition metal in the oxidation state 0 is present in the platinum catalyst in addition to Pt, then the metals can be present in the form of particles of pure metal or in the form of alloy particles. For the production of platinum catalysts which comprise, in addition to Pt, at least one further transition metal in the oxidation state 0, for example Ag, the open-pored support material can be impregnated within the context of the process according to the invention, for example, with platinum sulphite acid and with a further corresponding transition metal compound, before the metal components are converted into the oxidation state 0.

It is pointed out that the catalysts obtainable by the route of the process according to the invention are not limited to catalysts in which only Pt is present as the metal. It is also conceivable that sparingly reducible metals are also present in addition to platinum.

In one step of the process according to the invention, the open-pored support material is impregnated with platinum sulphite acid. Platinum sulphite acid is known in the prior art and is often referred to therein as "PSA". Platinum sulphite acid has the Chemical Abstract Number 61420-92-6 and is freely available commercially, for example from Heraeus, Hanau, Germany as 10.4% platinum sulphite acid solution.

In the process according to the invention the platinum sulphite acid is preferably used in the form of an aqueous platinum sulphite acid solution containing from 0.01 to 15% by weight of Pt (metal). It is further preferred to use the platinum sulphite acid in the process according to the invention in the form of an aqueous platinum sulphite acid solution containing from 0.1 to 8% by weight of Pt (metal), more preferably in the form of an aqueous platinum sulphite acid solution containing from 1 to 6% by weight of Pt (metal) and particularly preferably in the form of an aqueous platinum sulphite acid solution containing from 2.5 to 3.5% by weight of Pt (metal). It is most preferred to use the platinum sulphite acid in the process according to the invention in the form of an aqueous platinum sulphite acid solution containing from 2.8 to 3.3% by weight of Pt (metal).

According to a preferred embodiment of the process according to the invention, the process further comprises the step: conversion of the platinum component of the calcined platinum sulphite acid into the oxidation state 0. The support material impregnated with platinum sulphite acid is thereby subjected, after the calcination, to a reduction step. In the event that the process according to the invention comprises the abovementioned step of conversion of the platinum component of the calcined platinum sulphite acid into the oxidation state 0, the process according to the invention relates to a process for the production of a supported platinum catalyst, wherein the platinum catalyst can comprise, in addition to Pt in the oxidation state 0, one or more further transition metals, in particular noble metals, in the oxidation state 0.

The conversion of the platinum component of the calcined platinum sulphite acid into the oxidation state 0 can take place both by the wet chemical route, that is to say by means of a solution having a reducing action, and by the dry chemical route, that is to say by means of a gas having a reducing action. It is preferred according to the invention that the conversion of the platinum component of the calcined platinum sulphite acid into the oxidation state 0 takes place by the dry chemical route. This provides the possibility of carrying out the reduction at comparatively high temperatures in a manner which is simple in terms of the process, which facilitates a rapid and complete reduction of the platinum component.

According to a further preferred embodiment of the process according to the invention it is provided that the conversion of the platinum component of the calcined platinum sulphite acid into the oxidation state 0 is carried out at a temperature of at least 100°C. In this connection it is preferred that the reduction of the platinum component is carried out at a temperature of from 100°C to 400°C, more preferably at a temperature of from 200°C to 350°C, further preferably at a temperature of from 275°C to 325°C and particularly preferably at a temperature of 300°C.

As has already been stated above, it can be preferred according to the invention that the conversion of the platinum component of the calcined platinum sulphite acid into the oxidation state 0 is carried out by the dry chemical route. There can be used in principle any gaseous or gasifiable reducing agent by means of which the platinum component can be reduced, such as, for example, hydrogen, carbon monoxide, ethene or methanol, ethanol, etc. According to a particularly preferred embodiment of the process according to the invention it is provided that the conversion of the platinum component of the calcined platinum sulphite acid into the oxidation state 0 is carried out by means of hydrogen.

If hydrogen is used as the reducing agent, it can be preferred that the hydrogen is diluted with an inert gas such as, for example, nitrogen or a noble gas such as helium, neon, argon, krypton and/or xenon, nitrogen being particularly inexpensive and accordingly preferred according to the invention. It is preferred according to the invention, for example, to convert the platinum component of the calcined platinum sulphite acid into the oxidation state 0 by reduction under an atmosphere consisting of from 0.1% by weight to 100% by weight of hydrogen, preferably from 3 to 5% by weight of hydrogen, with the remainder being inert gas.

It is further preferred according to the invention, for example, to convert the platinum component of the calcined platinum sulphite acid into the oxidation state 0 by reduction under an atmosphere consisting of from 10% by weight to 60% by weight hydrogen, preferably from 15 to 30% by weight hydrogen, with the remainder being inert gas.

In order largely to minimize the content of sulphur in the platinum catalyst resulting from the process according to the invention, it can be provided according to a further preferred embodiment of the process according to the invention that the steps of calcination of the impregnated support material under protective gas and of conversion of the platinum component of the calcined platinum sulphite acid into the oxidation state 0 are carried out a plurality of times. For example, the two mentioned process steps can each be carried out 2, 3, 4 or 5 times, whereby after each calcination step the conversion of the platinum component into the oxidation state 0 is carried out.

Within the meaning of the present invention it is further preferred that the reduction is carried out for a duration of at least 1 minute, preferably at least 30 minutes, further preferably at least 1 hour and most preferably of at least 3 hours, a duration of 4 or 5 hours being most preferred.

The impregnation of the open-pored support material with platinum sulphite acid within the context of the present invention can in principle be carried out by any method which is known to the person skilled in the art from the prior art and is considered to be suitable. Examples of methods which are preferred according to the invention are the application of a platinum sulphite solution to the support material by spraying, the immersion of the support material in a platinum sulphite acid solution, or the so-called incipient wetness method (pore filling method), in which there is added to the support material a volume of solution corresponding to its pore volume.

If the application of the platinum sulphite acid solution is to be carried out by spraying the solution onto the support material, the spraying can be carried out according to the invention by any spray method known to the person skilled in the art from the prior art.

If it is provided that the application of the platinum sulphite acid solution is to be carried out by immersion of the support material in the solution, this is carried out by first immersing the support material in the platinum sulphite acid solution and then freeing the support material of solution that has not adhered to the support material surface – for example by removal by suction.

It is particularly preferred according to the invention that the impregnation of the support material with platinum sulphite acid is carried out by means of the incipient wetness method. In this method, the open-pored support material is loaded with a solution of the impregnating agent – here platinum sulphite acid – the volume of the solution corresponding to the pore volume of the support material, which is why the zeolite material is dry on the outside and thus pourable after being loaded with the solution. The incipient wetness method is also known to the person skilled in the art by the name pore filling method.

The open-pored support material of the present invention is any support material which is known to the person skilled in the art as being suitable for the purpose according to the invention. The open-pored support material is preferably an inorganic open-pored support material.

It is further preferred that the open-pored support material is a support material with monomodal or with polymodal pore distribution.

In accordance with a further preferred embodiment of the process according to the invention, the support material comprises a material selected from the group consisting of titanium oxide; γ-, θ- or Δ-aluminium oxide; cerium oxide; silicon oxide; zinc oxide; magnesium oxide; aluminium-silicon oxide; silicon carbide and magnesium silicate or a mixture of two or more of the abovementioned materials. It can further be preferred that the support material consists of one of the abovementioned materials or mixtures.

According to a further preferred embodiment of the process according to the invention it is provided that the support material is a zeolite material. Within the context of the present invention a zeolite material is understood as being, according to a definition of the International Mineralogical Association (D.S. Coombs *et al.*, Can. Mineralogist, 35, 1997, 1571), a crystalline substance with a structure characterized by a lattice of interconnected tetrahedrons. Each tetrahedron consists of four oxygen atoms which surround a central atom, the lattice containing open voids in the form of channels and cages, which are normally occupied by water molecules and extra-lattice cations, which can frequently be exchanged. The channels of the material are large enough to allow access to guest compounds. In the case of the hydrated materials, dehydration takes place mostly at temperatures below about 400°C and is for the most part reversible.

According to a further preferred embodiment of the process according to the invention it is provided that the zeolite material is a microporous or mesoporous zeolite material. In accordance with the classification of porous solids according to IUPAC (International Union of Pure and Applied Chemistry), the expressions "microporous zeolite material" and "mesoporous zeolite material" are to be understood as meaning zeolite materials whose pores have a diameter of less than 2 nm or a diameter of from 2 nm to 50 nm, respectively.

The zeolite material to be used in the process according to the invention can preferably correspond to one of the following structure types: ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOG, BPH, BRE, CAN, CAS, CDO, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EON, EPI, ERI, ESV, ETR, EUO, EZT, FAR, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, IHW, ISV, ITE, ITH, ITW, IWR, IWV, IWW, JBW, KFI,

LAU, LEV, LIO, LIT, LOS, LOV, LTA, LTL, LTN, MAR, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MOZ, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NES, NON, NPO, NSI, OBW, OFF, OSI, OSO, OWE, PAR, PAU, PHI, PON, RHO, RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBS, SBT, SFE, SFF, SFG, SFH, SFN, SFO, SGT, SIV, SOD, SOS, SSY, STF, STI, STT, SZR, TER, THO, TON, TSC, TUN, UEI, UFI, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, WEN, YUG and ZON, zeolite materials of the structure type beta (BEA) being particularly preferred. The above three-letter code nomenclature corresponds to the "IUPAC Commission of Zeolite Nomenclature".

Likewise preferred according to the invention are the members of mesoporous zeolite materials of the family which are subsumed in the literature under the name "MCM", this designation not referring to a specific structure type (see http://www.iza-structure.org/databases). Particularly preferred according to the invention are mesoporous silicates which are referred to as MCM-41 or MCM-48. MCM-48 has a 3D structure of mesopores, so that the catalytically active metal in the pores is particularly readily accessible. MCM-41 is particularly preferred and has a hexagonal arrangement of mesopores of uniform size. The MCM-41 zeolite material has an SiO_2/Al_2O_3 molar ratio of preferably greater than 100, more preferably of greater than 200 and most preferably of greater than 300. Further preferred mesoporous zeolite materials which can be used within the context of the present invention are those which are referred to in the literature as MCM-1, MCM-2, MCM-3, MCM-4, MCM-5, MCM-9, MCM-10, MCM-14, MCM-22, MCM-35, MCM-37, MCM-49, MCM-58, MCM-61, MCM-65 or MCM-68.

Which zeolite material is to be used in the process according to the invention depends primarily on the intended use of the catalyst that is to be produced by means of the process according to the invention. A large number of methods are known in the prior art for tailoring the properties of zeolite materials, for example the structure type, the pore diameter, the channel diameter, the chemical composition, the ion exchange capacity and the activation properties, to a corresponding intended use.

The zeolite material to be used in the process according to the invention can be, for example, a silicate, an aluminium silicate, an aluminium phosphate, a silicon aluminium phosphate, a metal aluminium phosphate, a metal aluminium phosphosilicate, a gallium aluminium silicate, a gallium silicate, a boroaluminium silicate, a borosilicate or a titanium silicate, particular preference being given to aluminium silicates and titanium silicates.

According to the definition of the International Mineralogical Association (D.S. Coombs *et al.*, Can. Mineralogist, 35, 1997, 1571), the expression "aluminium silicate" is understood as meaning a crystalline substance with a spatial lattice structure of the general formula $M^{n+}[(AlO_2)_x(SiO_2)_y]xH_2O$, which are composed of $SiO_{4/2}$ and $AlO_{4/2}$ tetrahedrons which are linked by common oxygen atoms to form a regular three-dimensional lattice. The atomic ratio of $Si/Al = y/x$ is always greater than/equal to 1 according to the so-called "Löwenstein's rule", which forbids the adjacent occurrence of two adjacent negatively charged $AlO_{4/2}$ tetrahedrons. Although, at a low Si/Al atomic ratio, more exchange sites for metals are thus available, the zeolite becomes increasingly more thermally unstable.

Within the context of the present invention, the abovementioned zeolite materials can be used in the process both in the alkali form, for example in the Na and/or K form, and in the alkaline earth form, ammonium form or in the H form. In addition, it is also possible to use the zeolite material in a mixed form.

In accordance with a further preferred embodiment of the process according to the invention it can be provided that a drying step is carried out between step a) and step b).

The drying step is carried out between the impregnation and the calcination. The drying temperature is preferably between 25°C and 250°C, more preferably between 50°C and 200°C, further preferably between 100°C and 180°C and particularly preferably at 120°C.

Drying is carried out preferably over a period of more than 1 minute, more preferably over a period of more than 1 hour, further preferably over a period of more than 5 hours and yet more preferably over a period of more than 12 hours, wherein a drying time of 10 hours can be particularly preferred. In this connection, it can additionally be advantageous if the duration of the drying step does not exceed a period of 48 hours, preferably does not exceed a period of 24 hours.

The term "calcination" is generally understood as meaning heating at high temperatures with the aim of changing the treated material or a component thereof, for example, materially or structurally. By means of calcination it is possible to achieve, for example, thermal degradation, a phase transition or the removal of volatile substances.

Within the context of the present invention, the calcination is carried out preferably in a temperature range of from 300°C to 1200°C, more preferably in a temperature range of from 300°C to 1000°C, further preferably in a temperature range of from 400°C to 950°C, particularly preferably in a temperature range of from 700 to 900°C and most preferably in a temperature range of from 730°C to 900°C.

It is moreover particularly preferred that the calcination is carried out at a temperature of at least 750°C. With calcination at a temperature of at least 750°C it is possible by means of the process according to the invention to obtain supported platinum catalysts which, despite a high platinum loading of, for example, 3% by weight, based on the weight of the platinum and of the open-pored support material, are largely free of sulphur. Thus, for example, it is possible to produce by means of the process according to the invention platinum catalysts which comprise from 1 to 5% by weight of platinum, based on the weight of the platinum and of the support material, and have a sulphur content of less than 0.004% by weight, based on the weight of the platinum and of the support material. A low content of sulphur is particularly advantageous because sulphur acts as a catalyst poison in particular in respect of noble metals.

The heating rate in the calcination is preferably from 0.5°C/min to 5°C/min, more preferably from 1°C/min to 4°C/min and particularly preferably 2°C/min.

The duration of the calcination at maximum temperature is preferably in a range of from 1 minute to 48 hours, more preferably in a range of from 30 minutes to 12 hours and particularly preferably in a range of from 1 hour to 7 hours, a calcination time of 5 hours or 6 hours being particularly preferred.

Within the context of the present invention, the calcination is carried out under a protective gas. Protective gas is understood as meaning gases or gas mixtures which can be used as an inert protecting atmosphere, for example in order to avoid undesirable chemical reactions. Within the context of the present invention there can be used as protective gas in particular the noble gases helium, neon, argon, krypton or xenon or mixtures of two or more of the abovementioned gases, argon being particularly preferred as the protective gas. As well as the noble gases or in addition thereto, nitrogen, for example, can also be used as a protective gas.

A typical process provided by the present invention comprises the steps:

a) impregnation of an open-pored support material, in particular of a zeolite material of the structure type BEA or of a zeolite material from the MCM family, preferably of an aluminium silicate or titanium silicate zeolite material, with platinum sulphite acid, in particular with a platinum sulphite acid solution, preferably by the incipient wetness method;

b) calcination, preferably at a temperature above 750°C, of the impregnated support material under protective gas, preferably under argon;

c) optional conversion of the platinum component of the calcined platinum sulphite acid into the oxidation state 0, preferably by reduction by means of hydrogen, preferably at a temperature of at least 100°C.

The present invention relates further to a catalyst precursor or to a catalyst obtainable by the process according to the invention. By means of the process according to the invention it is possible to obtain supported platinum catalysts which, compared with the corresponding platinum catalysts known in the prior art, are distinguished by increased activity and by increased thermal ageing resistance, or catalyst precursors which can be converted into platinum catalysts having the mentioned advantages.

The present invention relates in particular to a catalyst precursor obtainable by a process comprising the steps:

a) impregnation of an open-pored support material, in particular of a zeolite material, preferably of a zeolite material of the structure type BEA or of a zeolite material from the MCM family, with platinum sulphite acid by the incipient wetness method;

b) drying of the impregnated support material over a period of 12 hours at a temperature of 120°C;

c) calcination of the impregnated and dried support material over a period of 5 hours at 790°C under argon.

The present invention additionally relates in particular to a supported Pt catalyst obtainable by a process comprising the steps:

a) impregnation of an open-pored support material, in particular of a zeolite material, preferably of a zeolite material of the structure type BEA or of a zeolite material from the MCM family, with platinum sulphite acid by the incipient wetness method;

b) drying of the impregnated support material over a period of 12 hours at a temperature of 120°C;

c) calcination of the impregnated and dried support material over a period of 5 hours at 790°C under argon;

d) conversion of the platinum component of the calcined platinum sulphite acid into the oxidation state 0 by reduction of the platinum component by means of a gas consisting of 5% by volume of hydrogen in nitrogen over a period of 5 hours at a temperature of 300°C.

The present invention relates further to a catalyst comprising an open-pored support material, which is preferably a zeolite material, as well as platinum in the oxidation state 0, wherein the XRD spectrum of the catalyst is free of signals of elemental platinum. Such catalysts can be produced by means of the process according to the invention. It is supposed that the XRD spectrum of the catalyst is free of Pt signals because the outer surface of the support material is substantially free or completely free of metal particles of a size which can bend X-radiation according to the diffraction pattern of platinum.

According to a definition of the International Mineralogical Association (D.S. Coombs *et al.*, Can. Mineralogist, 35, 1997, 1571), the zeolite material of the catalyst according to the invention can be understood as being a crystalline substance with a structure characterized by a lattice of interconnected tetrahedrons. Each tetrahedron consists of four oxygen atoms which surround a central atom, the lattice containing open voids in the form of channels and cages, which are normally occupied by water molecules and extra-lattice cations, which can frequently be exchanged. The channels of the material are large enough to allow access to guest compounds. In the case of the hydrated materials, dehydration takes place mostly at temperatures below about 400°C and is for the most part reversible.

According to a further preferred embodiment of the catalyst according to the invention it is provided that the zeolite material is a microporous or mesoporous zeolite material. In accordance with the classification of porous solids according to IUPAC (International Union of Pure and Applied Chemistry), the expressions "microporous zeolite material" and "mesoporous zeolite material" are to be understood as meaning zeolite materials whose pores have a diameter of less than 2 nm or a diameter of from 2 nm to 50 nm, respectively.

The zeolite material of the catalyst according to the invention can preferably correspond to one of the following structure types: ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOG, BPH, BRE, CAN, CAS, CDO, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EON, EPI, ERI, ESV, ETR, EUO, EZT, FAR, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, IHW, ISV, ITE, ITH, ITW, IWR, IWV, IWW, JBW, KFI, LAU, LEV, LIO, LIT, LOS, LOV, LTA, LTL, LTN, MAR, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MOZ, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NES, NON, NPO, NSI, OBW, OFF, OSI, OSO, OWE, PAR, PAU, PHI, PON, RHO, RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBS, SBT, SFE, SFF, SFG, SFH, SFN, SFO, SGT, SIV, SOD, SOS, SSY, STF, STI, STT, SZR, TER, THO, TON, TSC, TUN, UEI, UFI, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, WEN, YUG and ZON, zeolite materials of the structure type beta (BEA) being particularly preferred. The above three-letter code nomenclature corresponds to the "IUPAC Commission of Zeolite Nomenclature".

Likewise preferred according to the invention are the members of mesoporous zeolite materials of the family which are subsumed in the literature under the name "MCM", this designation not referring to a specific structure type (see http://www.iza-structure.org/databases). Particularly preferred according to the invention are mesoporous silicates which are referred to as MCM-41 or MCM-48. MCM-48 has a 3D structure of mesopores, so that the catalytically active metal in the pores is particularly readily accessible. MCM-41 is particularly preferred and has a hexagonal arrangement of mesopores of uniform size. The MCM-41 zeolite material has an SiO_2/Al_2O_3 molar ratio of preferably greater than 100, more preferably of greater than 200 and most preferably of greater than 300. Further preferred mesoporous zeolite materials which can be used within the context of the present invention are those which are referred to in the literature as MCM-1, MCM-2, MCM-3, MCM-4, MCM-5, MCM-9, MCM-10, MCM-14, MCM-22, MCM-35, MCM-37, MCM-49, MCM-58, MCM-61, MCM-65 or MCM-68.

Which zeolite material is contained in the catalyst according to the invention depends primarily on the intended use of the catalyst according to the invention. A large number of methods are known in the prior art for tailoring the properties of zeolite materials, for example the structure type, the pore diameter, the channel diameter, the chemical composition, the ion exchange capacity and the activation properties, to a corresponding intended use.

The zeolite material of the catalyst according to the invention can be, for example, a silicate, an aluminium silicate, an aluminium phosphate, a silicon aluminium phosphate, a metal aluminium phosphate, a metal aluminium phosphosilicate, a gallium aluminium silicate, a gallium silicate, a boroaluminium silicate, a borosilicate or a titanium silicate, particular preference being given to aluminium silicates and titanium silicates.

According to the definition of the International Mineralogical Association (D.S. Coombs *et al.*, Can. Mineralogist, 35, 1997, 1571), the expression "aluminium silicate" is understood as meaning a crystalline substance with a spatial lattice structure of the general formula $M^{n+}[(AlO_2)_x(SiO_2)_y]xH_2O$, which are composed of $SiO_{4/2}$ and $AlO_{4/2}$ tetrahedrons which are linked by common oxygen atoms to form a regular three-dimensional lattice. The atomic ratio of Si/Al = y/x is always greater than/equal to 1 according to the so-called "Löwenstein's rule", which forbids the adjacent occurrence of two adjacent negatively charged $AlO_{4/2}$ tetrahedrons. Although, at a low Si/Al atomic ratio, more exchange sites for metals are thus available, the zeolite becomes increasingly more thermally unstable.

The abovementioned zeolite materials can be present in the catalyst according to the invention both in the alkali form, for example in the Na and/or K form, and in the alkaline earth form, ammonium form or in the H form. In addition, it is also possible that the zeolite material is present in a mixed form, for example in an alkali/alkaline earth mixed form.

The catalyst according to the invention comprises from 1 to 10% by weight of platinum, based on the weight of the platinum and of the support material. It has been found that, by means of the process according to the invention, there are obtainable supported platinum catalysts whose XRD spectra are free of signals of platinum despite the comparatively high platinum loading and which have a high thermal ageing resistance despite the comparatively high platinum loading. Moreover, it can be provided in this connection according to a preferred embodiment of the catalyst according to the invention that the catalyst, based on the weight of the platinum and of the support material, comprises from 2 to 5% by weight of platinum, further preferably from 2.2 to 4.5% by weight, particularly preferably from 2.5 to 3.5% by weight and most preferably 3% by weight.

In accordance with a further preferred embodiment of the catalyst according to the invention it is provided that the catalyst is free of further metals in the oxidation state 0.

As already stated above, the support material, according to a preferred embodiment of the catalyst according to the invention, is a zeolite material of the structure type beta or a zeolite material from the MCM family.

Furthermore, according to a further preferred embodiment of the catalyst according to the invention it can be provided that the BET surface area of the zeolite material is from 100 to 1500 m^2/g, preferably from 150 to 1000 m^2/g and more preferably from 200 to 600 m^2/g. The BET surface area is to be determined by the one-point method by adsorption of nitrogen in accordance with DIN 66132.

According to a further preferred embodiment of the catalyst according to the invention it can be provided that the catalyst is in the form of a powder, a shaped body or a monolith. Preferred shaped bodies are spheres, rings, cylinders, perforated cylinders, trilobes or cones and a preferred monolith is, for example, a honeycomb body.

The dispersion of a supported metal catalyst is understood as being the ratio of the number of all the surface metal atoms of all the metal particles of a support to the total number of all the metal atoms of the metal particles. It is generally preferred if the dispersion value is comparatively high, since in this case as many metal atoms as possible are freely accessible for a catalytic reaction. That is to say, with a comparatively high dispersion value of a supported metal catalyst, a specific catalytic activity thereof can be achieved with a comparatively small amount of metal used. In accordance with a further preferred embodiment of the catalyst according to the invention, the dispersion of the platinum particles is from 50 to 100%, preferably from 55 to 90%, further preferably from 60 to 90%, particularly preferably from 75 to 85%. The values of the dispersion are thereby to be determined by means of hydrogen in accordance with DIN 66136-2.

In principle, it is advantageous if the platinum in the catalyst according to the invention is present as particles that are as small as possible, since the platinum particles then have a very high degree of dispersion. However, an advantageous mean particle diameter is also dependent on the application for which the catalyst is to be used, as well as on the pore distribution and in particular the pore radii and channel radii of the support material. According to a preferred embodiment of the catalyst according to the invention, the metal particles have a mean diameter which is smaller than the pore diameter and larger than the channel diameter of the support material. As a result, the metal particles are mechanically trapped in the support material, which leads to a high thermal ageing resistance of the catalyst according to the invention. For example, the metal particles have a mean diameter of from 0.5 to 5 nm, preferably a mean diameter of from 0.5 to 4 nm, more preferably a mean diameter of from 0.5 to 3 nm and particularly preferably a mean diameter of from 0.5 to 2 nm. The mean particle diameter is preferably to be determined by decomposition of the support material and measurement of the remaining Pt particles by means of transmission electron microscopy (TEM).

The present invention relates further to the use of a catalyst according to the invention in a catalysis process which is carried out above a temperature of 700°C.

In accordance with a preferred embodiment of the use according to the invention, the catalysis process is a purification of exhaust gases from industry or vehicles, such as preferably exhaust gases from cars, ships, trains, etc.

The examples which follow serve, in conjunction with the drawings, to explain the invention. In the drawings:

Fig. 1: shows an XRD spectrum of a first catalyst according to the invention produced by the process according to the invention (1) and of a first comparison catalyst (2);

Fig. 2: shows the propane conversion of the first catalyst (squares), of the first catalyst after ageing (circles) and of the first comparison catalyst (triangles) in the heating phase in dependence on the temperature;

Fig. 3: shows the propane conversion of the first catalyst (squares) and of the first comparison catalyst (triangles) in the temperature maintenance phase (550°C) in dependence on the time;

Fig. 4: shows the propane conversion of the first catalyst (squares) and of the first comparison catalyst (triangles) in the cooling phase in dependence on the temperature;

Fig. 5: shows XRD spectra (in part) of a second catalyst according to the invention produced by the process according to the invention (11) and of a second (13) and third (12) comparison catalyst;

Fig. 6: shows the propane conversion of the second catalyst according to the invention (11), of the second comparison catalyst (13) and of the third comparison catalyst (12) in the heating phase in dependence on the temperature.

Example 1:

A powdered aluminium silicate zeolite material (20 g) of the structure type beta (BEA) in the H form having an Si/A12 atomic ratio of 35 was impregnated with 21.9 ml of an aqueous platinum sulphite acid solution containing 3.2% by weight of Pt (calculated as metal) by means of the incipient wetness method. The water absorption of dry BEA is (at 120°C overnight) 9.2 g H_2O/10 g BEA. 12.96 g of H_2O were added to the PSA solution. The solution had a Pt concentration of 3.2% by weight (the impregnation was carried out using this solution).
After the impregnation, the zeolite material was dried overnight at a temperature of 120°C.
After drying, the impregnated zeolite material was calcined over a period of 5 hours at a temperature of 770°C under an argon atmosphere. The heating rate was 2°C/min and the argon volume flow during the heating and calcination phase was 2 l/min.

After the calcination, the zeolite material loaded with platinum was reduced over a period of 5 hours at a temperature of 300°C by means of a gas containing 5% by volume of hydrogen in nitrogen (2 l/min). The heating rate was 2°C/min.

Example 2:

The catalyst obtained according to Example 1 was calcined in the air for a period of 10 hours at a temperature of 650°C (heating rate: 10°C/min) for the purpose of ageing.

Comparison Example 1:

A catalyst was produced analogously to Example 1, with the only difference that the calcination was carried out in air.

XRD measurement 1:

The catalyst produced according to Example 1 and Comparison Example 1 was measured by X-ray diffractometry. The measured XRD spectra are shown in Figure 1, the spectrum of Example 1 and that of Comparison Example 1 being provided with the reference numerals 1 and 2, respectively.

The XRD spectrum of the catalyst produced according to Example 1 (calcination under argon) does not show any Pt signals, whereas the XRD spectrum of the catalyst produced according to Comparison Example 1 (calcination in the air) shows clear Pt signals. In fact, the signal at a 2 theta value of approximately 40° is the Pt(110) reflection (110 are the Miller indices), the signal at a 2 theta value of approximately 46.5° is the Pt(200) reflection.

The absence of Pt reflections in the case of the catalyst according to Example 1 is an indication that, despite the comparatively high calcination temperature, no larger platinum clusters have formed on the outer surface of the zeolite material and the platinum is located in highly disperse form predominantly in the zeolite material.

Elemental analysis:

Within the context of an elemental analysis which was performed it was found that the catalyst according to Example 1 has a content of sulphur of less than 0.004% by weight, whereas the catalyst produced according to Comparison Example 1 has a content of sulphur of 0.155% by weight.

Activity test 1:

The catalysts produced according to Examples 1 and 2 and also the catalyst produced according to Comparison Example 1 were subjected to a conversion of propane as an activity test under the following test conditions.

Test conditions:

Particle size:	0.5-1.25 mm
Temperature profile:	Room temperature (RT) → 550°C (5 hours) → RT
Heating rate:	10°C/min
Cooling rate:	20°C/min
CO concentration:	800 ppm
Propane concentration:	200 ppm
Gas hourly space velocity (GHSV):	100,000 h^{-1}
Weighed portion:	7 g
Catalyst volume:	14 ml

Figure 2 shows the curve profiles of the measured propane conversions in the heating phase in dependence on the temperature, Figure 3 shows the curve profiles of the propane conversions during the temperature maintenance phase in dependence on the time, and Figure 4 shows the curve profiles of the propane conversions in the cooling phase in dependence on the temperature, the curve profiles of the catalysts of Examples 1 and 2 and of

Comparison Example 1 being marked by squares, circles and triangles, respectively.

In the heating phase, the two catalysts according to Example 1 and Comparison Example 1 exhibit the same activity and achieve a conversion of about 95% (Figure 2). During the temperature maintenance phase, the activity of the catalyst calcined in air according to Comparison Example 1 falls significantly, whereas the catalyst calcined under argon according to Example 1 exhibits virtually the same activity over the entire temperature maintenance phase (Figure 3). In the cooling phase, the catalyst according to Example 1 likewise exhibits increased activity compared with the catalyst of Comparison Example 1 (Figure 4). The curve profiles for the catalyst according to Example 1 are almost identical in the heating phase and in the cooling phase (Figures 2 and 4).

The thermally aged catalyst according to Example 2 exhibits a significantly reduced activity in the low temperature range but at a temperature of 550°C achieves the conversion of the catalyst according to Example 1 that has not been aged (Figure 2). The

Comparison Example 2:

20 g of powdered aluminium silicate zeolite material of the structure type MFI (ZSM-5) in the ammonium form having an Si/Al atomic ratio of 27 were impregnated with 3% by weight of platinum (calculated as metal and based on the weight of the zeolite material and of the platinum) in the form of $(NH_3)_4Pt(NO_3)_2$ by means of the incipient wetness method.

After the impregnation, the zeolite material was dried overnight at a temperature of 120°C.

After drying, the impregnated zeolite material was calcined over a period of

5 hours at a temperature of 790°C under an argon atmosphere. The heating rate from room temperature to 300°C was 0.3°C/min, the heating rate from 300°C to 790°C was 4°C/min, and the argon volume stream during the heating and calcination phase was 2 l/min. The decomposition of the $(NH_3)_4Pt(NO_3)_2$ proceeds reductively, so that Pt in the oxidation state 0 forms in the calcination.

Comparison Example 3:

A catalyst was produced analogously to Comparison Example 2, with the only difference that a powdered aluminium silicate zeolite material of the structure type beta (BEA) in the H form with an Si/Al2 atomic ratio of 35 was used as the zeolite material.

Example 3:

A catalyst was produced analogously to Comparison Example 2 with the differences that a powdered aluminium silicate zeolite material of the structure type beta (BEA) in the H form with an Si/Al2 atomic ratio of 35 was used as the zeolite material, the heating rate from room temperature to 790°C was 2°C/min and, after the calcination, the zeolite material loaded with platinum was reduced over a period of 5 hours at a temperature of 300°C by means of a gas containing 5% by volume of hydrogen in nitrogen (2 l/min). The heating rate was 2°C/min.

XRD measurement 2:

The catalyst produced according to Example 3 and the catalysts produced according to Comparison Examples 2 and 3 were measured by X-ray diffractometry. The measured XRD spectra are shown in part in Figure 5, the spectrum of Example 3 and those of Comparison Examples 2 and 3 being provided with the reference numerals 11, 13 and 12, respectively.
The XRD spectrum of the catalyst produced according to Example 3 does not show any Pt reflections at a 2 theta value of approximately 40°, whereas the XRD

spectra of the catalysts produced according to Comparison Examples 2 and 3 show clear Pt reflections. In fact, the signal at a 2 theta value of approximately 40° is the Pt(110) reflection.

The absence of Pt reflections in the case of the catalyst according to Example 3 is an indication that no larger platinum particles have formed on the outer surface of the zeolite material and the platinum is located in highly disperse form predominantly in the zeolite material.

Activity test 2:

The catalyst produced according to Example 3 and also the catalysts produced according to Comparison Examples 2 and 3 were subjected to a conversion of propane as an activity test under the following test conditions.

Test conditions:

Particle size:	0.5-1.25 mm
Temperature profile:	Room temperature (RT) → 550°C
Heating rate:	10°C/min
CO concentration:	800 ppm
Propane concentration:	200 ppm
Gas hourly space velocity (GHSV):	100,000 h^{-1}
Weighed portion:	7 g
Catalyst volume:	14 ml

Figure 6 shows the curve profiles of the measured propane conversions in the heating phase in dependence on the temperature, the curve profile of the catalyst according to Example 3 and also those according to Comparison Examples 2 and 3 being provided with reference numerals 11, 13 and 12, respectively. The activity test clearly shows the increased activity of the catalyst according to the invention produced by means of the process according to the invention.

Patentkrav

1. Fremgangsmåde, omfattende trinnene:
a) imprægnering af et åbenporet bærermateriale med platinsulfitsyre;
b) kalcinering af det imprægnerede bærermateriale under en beskyttelsesgas.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** fremgangsmåden endvidere omfatter trinnet:
overførsel af platinkomponenten af den kalcinerede platinsulfitsyre til oxidationstrinnet 0.

3. Fremgangsmåde ifølge krav 2, **kendetegnet ved, at** overførslen af platinkomponenten af den kalcinerede platinsulfitsyre til oxidationstrinnet 0 foregår ved en temperatur på mindst 100 °C.

4. Fremgangsmåde ifølge krav 2 eller 3, **kendetegnet ved, at** overførslen af platinkomponenten af den kalcinerede platinsulfitsyre til oxidationstrinnet 0 foregår ved hjælp af hydrogen.

5. Fremgangsmåde ifølge et af kravene 2 til 4, **kendetegnet ved, at** trinnene med kalcinering af det imprægnerede bærermateriale under beskyttelsesgas og overførslen af platinkomponenten af den kalcinerede platinsulfitsyre til oxidationstrinnet 0 udføres flere gange.

6. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** imprægneringen foregår ved hjælp af Incipient-Wetness-metoden.

7. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** bærermaterialet er et uorganisk bærermateriale, udvalgt fra gruppen bestående af titaniumoxid; γ-, θ- eller Δ-aluminiumoxid; ceroxid; siliciumoxid; zinkoxid; magnesiumoxid; aluminium-siliciumoxid; siliciumcarbid og magnesiumsilikat, en blanding af to eller flere af de ovenfor nævnte materialer eller et mikroporøst eller mesoporøst zeolithmateriale.

8. Fremgangsmåde ifølge krav 7, **kendetegnet ved, at** zeolithmaterialet er et zeolithmateriale af strukturtypen beta eller er fra MCM-familien.

9. Fremgangsmåde ifølge krav 7 eller 8, **kendetegnet ved, at** zeolithmaterialet er et aluminiumsilikat eller et titaniumsilikat.

10. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved**, at der udføres et tørretrin mellem trin a) og trin b).

11. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** kalcineringen foregår ved en temperatur på mindst 750 °C.

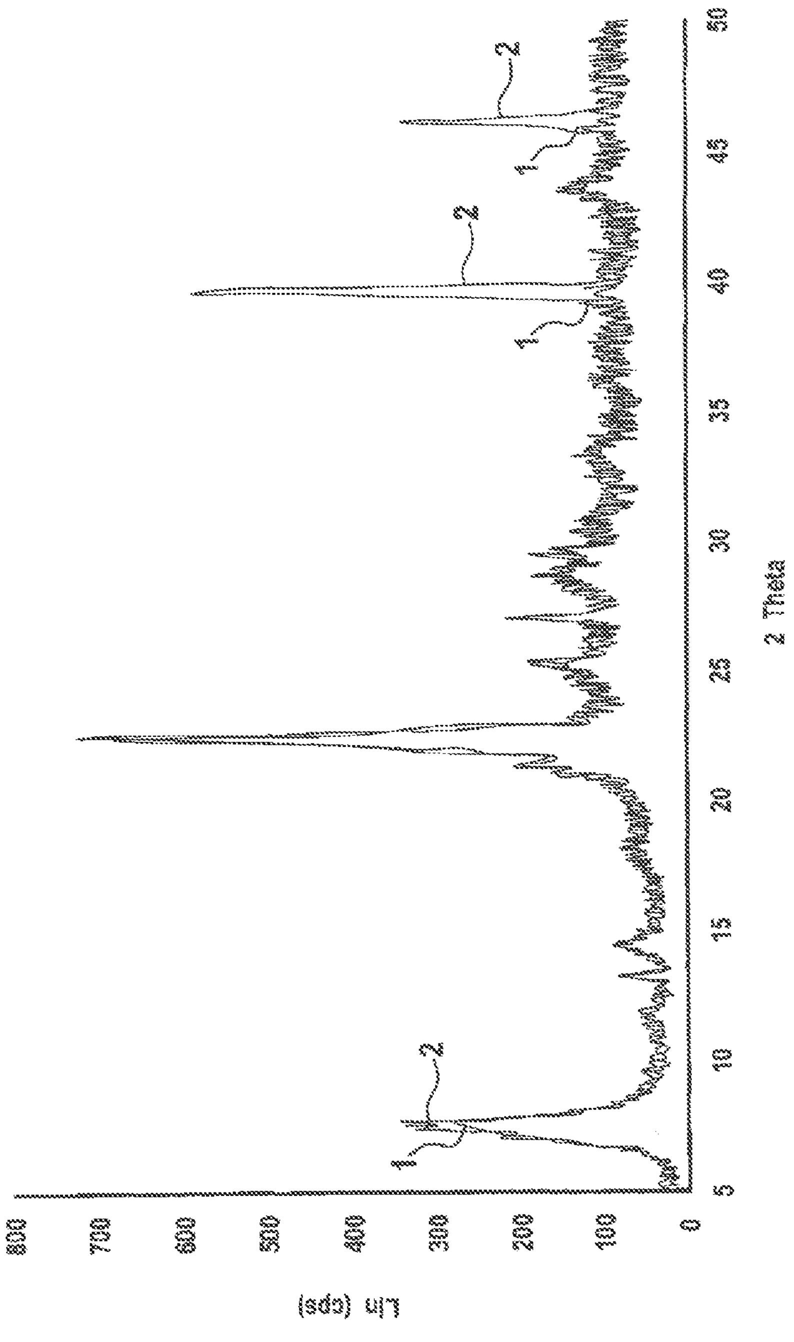
12. Katalysator-forstadium eller katalysator, der kan tilvejebringes i henhold til en fremgangsmåde ifølge et af kravene 1 til 11, **kendetegnet ved, at** katalysatoren omfatter 1 til 10 vægt-% platin, i forhold til platinets og bærermaterialets vægt.

13. Katalysator ifølge krav 12, omfattende platin fra oxidationstrinnet 0, **kendetegnet ved, at** katalysatorens XRD-spektrum er frit for signaler fra elementært platin, og at katalysatoren omfatter 1 til 10 vægt-% platin.

14. Katalysator ifølge krav 12 eller 13, **kendetegnet ved, at** katalysatoren omfatter 1 til 5 vægt-% platin.

15. Katalysator ifølge krav 13, **kendetegnet ved, at** bærermaterialet er et zeolithmateriale af strukturtypen beta.

16. Anvendelse af en katalysator ifølge et af kravene 12 til 15 i en katalyseproces, som udføres over en temperatur på 700 °C til rensning af udstødningsgasser fra industri eller køretøjer.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300
200
100
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2
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1
2

Fig. 1

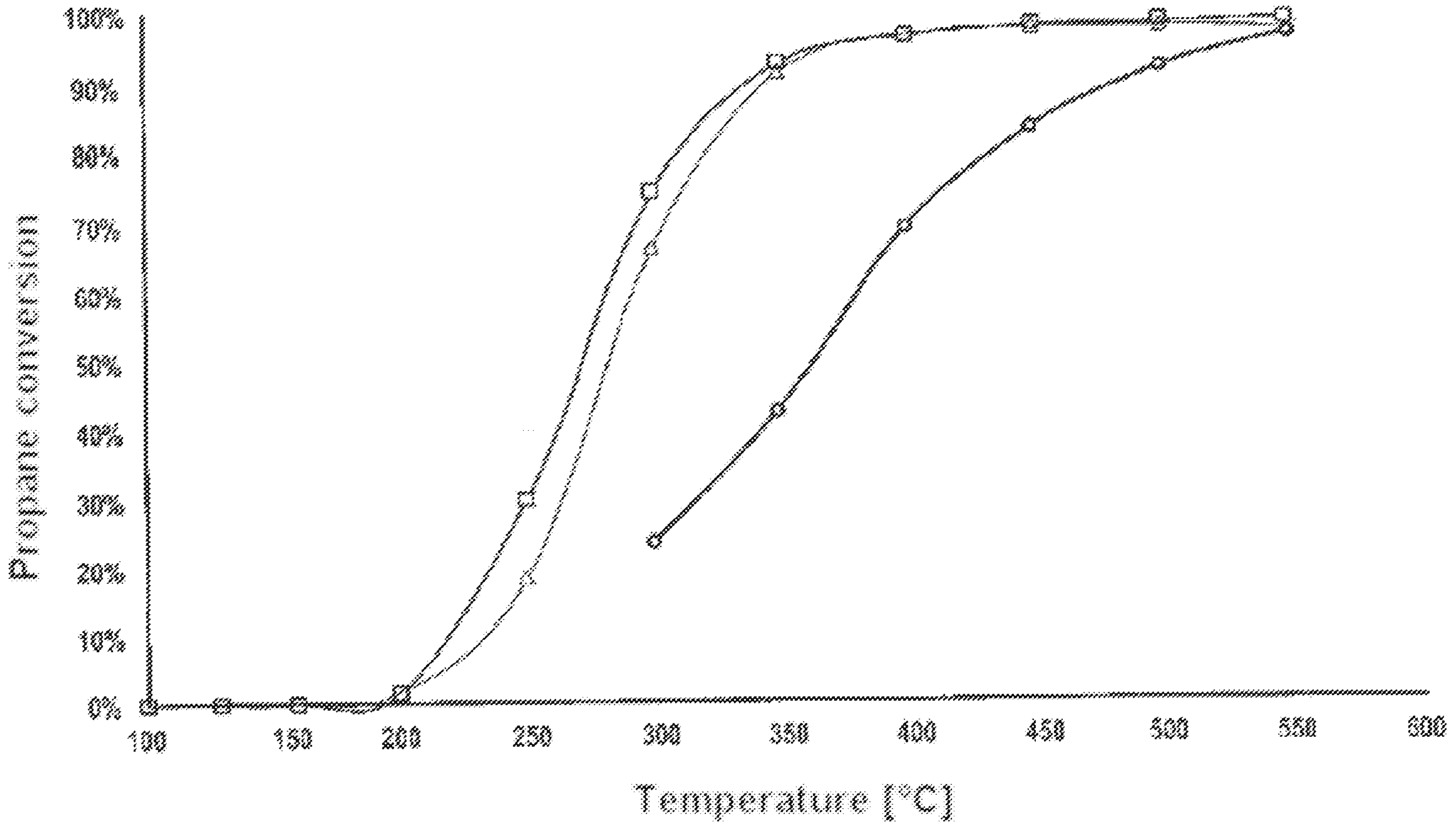

Propane conversion
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
100
150
200
250
300
350
400
450
500
550
600
Temperature [°C]

Fig. 2

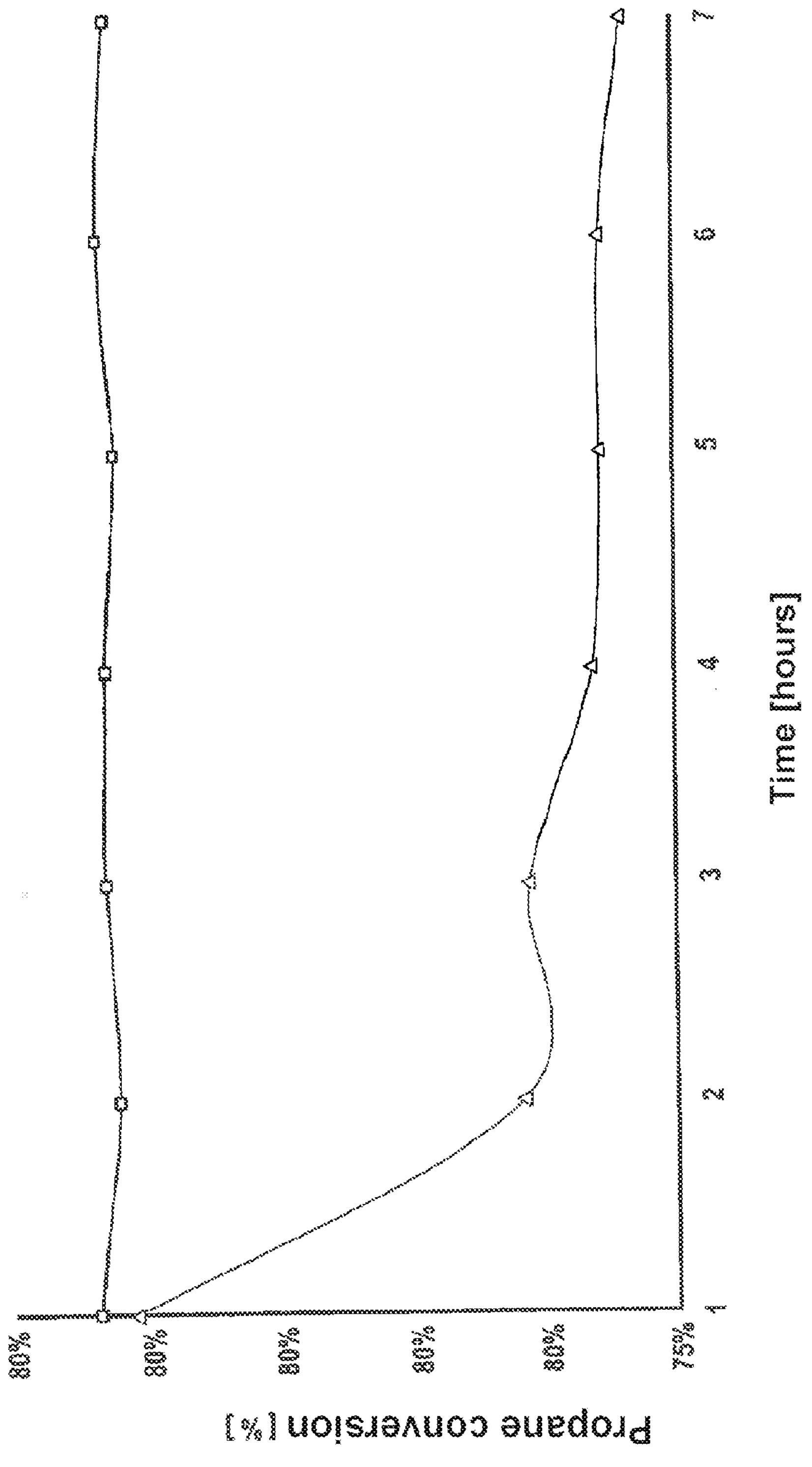


Fig. 3

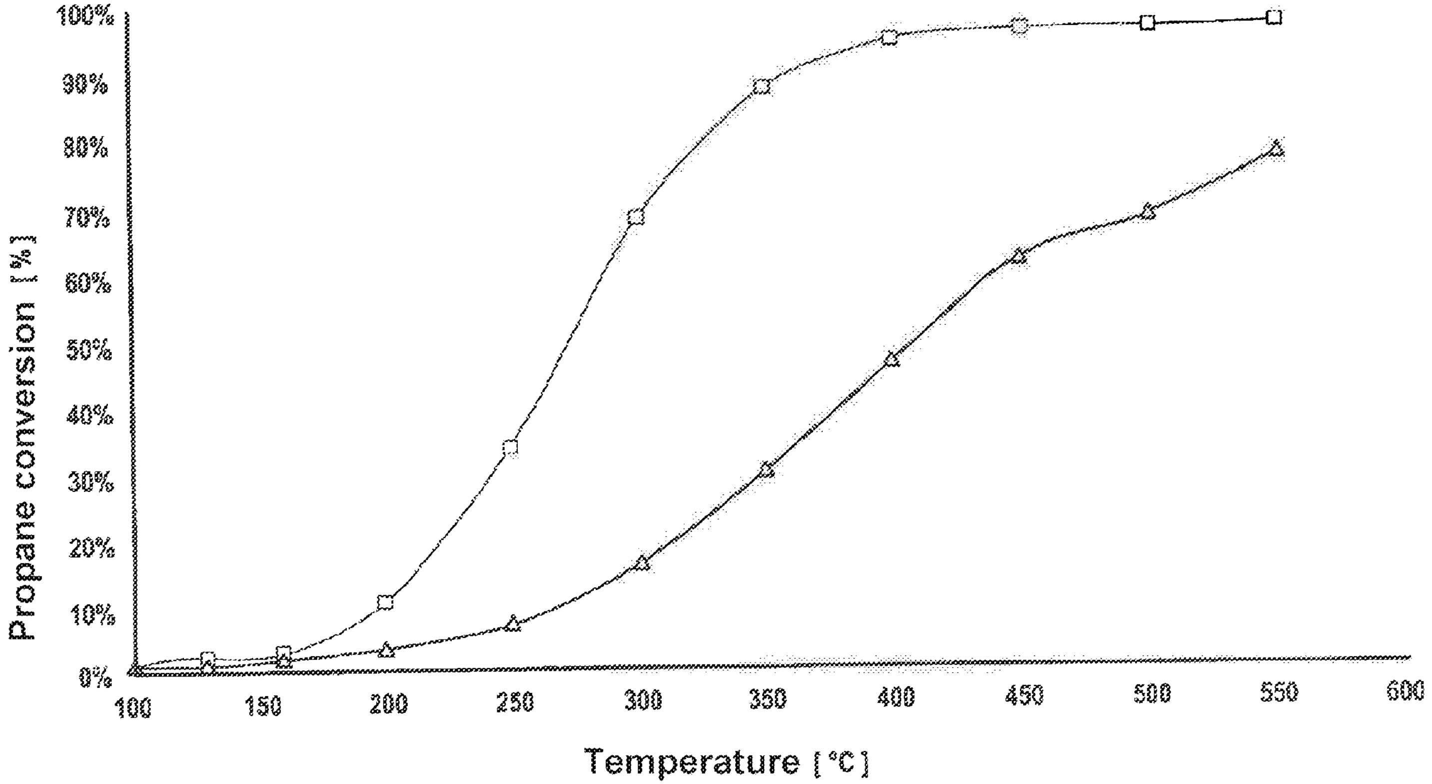
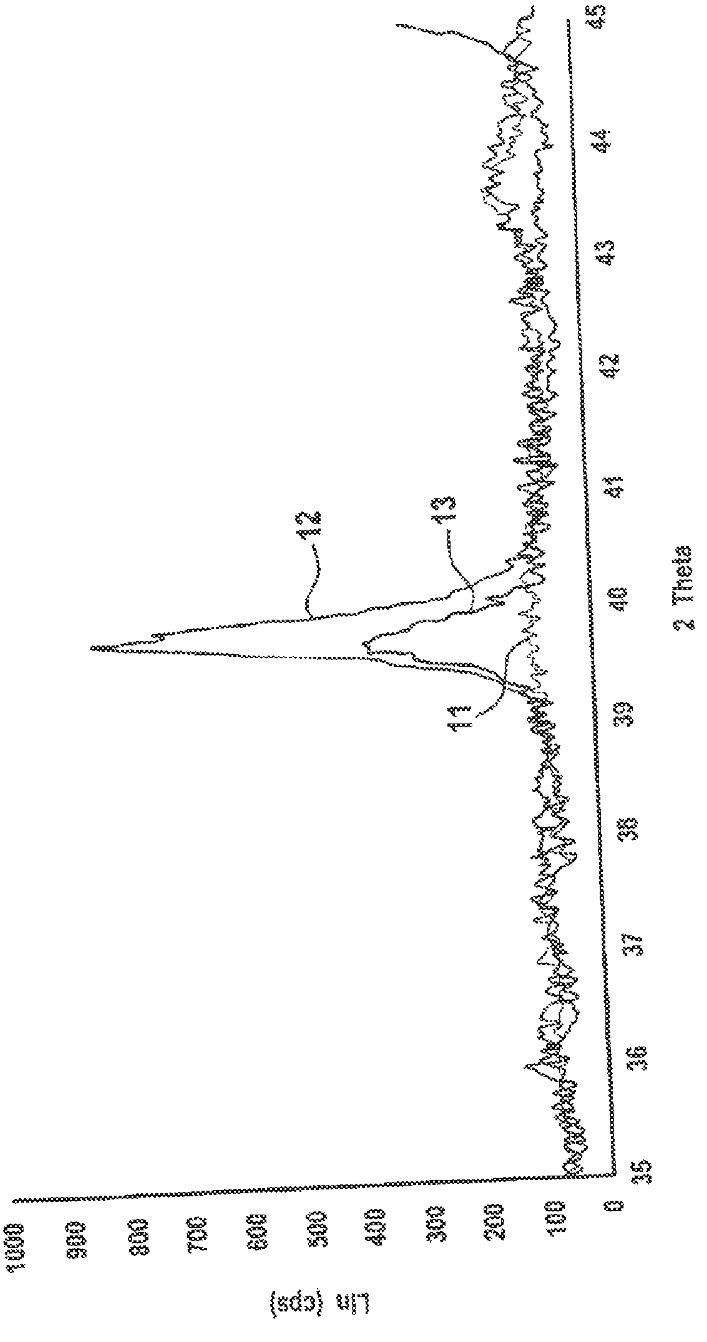

Propane conversion [%]
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
100
150
200
250
300
350
400
450
500
550
600
Temperature [°C]

Fig. 4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2 Theta
11
12
13

Fig. 5

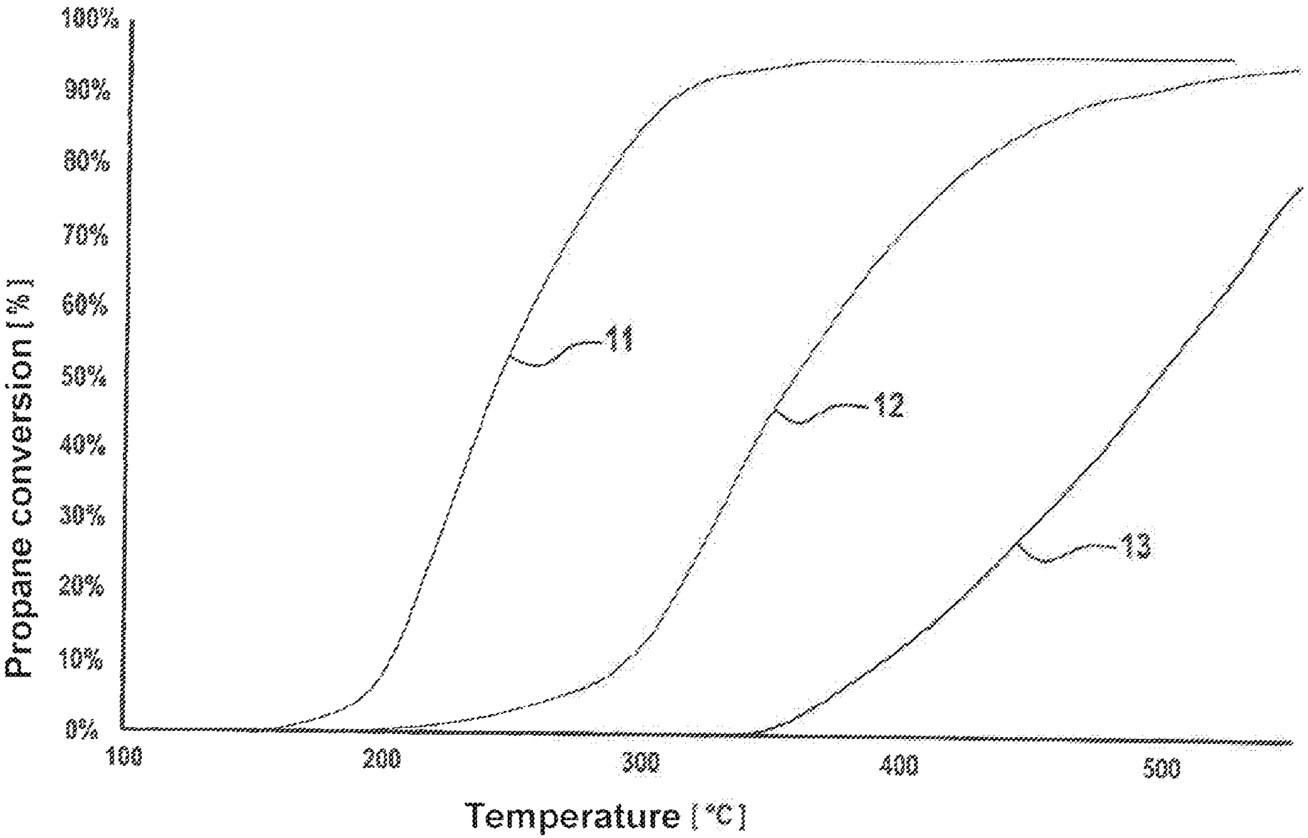
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Propane conversion [%]
100
200
300
400
500
Temperature [°C]
11
12
13

Fig. 6