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(54) Benævnelse: **BIMETALLISK ELLER MULTIMETALLISK KATALYSATOR MED ET OPTIMERET BIMETALLICITETSINDEKS OG EN OPTIMERET HYDROGENADSORPTIONSKAPACITET**

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Fortsættes ...

Description

FIELD OF THE INVENTION

The present invention relates to the field of hydrocarbon conversion and more specifically to the reforming of hydrocarbon feedstocks in the presence of a catalyst to produce gasoline cuts. The invention also relates to improved catalytic formulations based on a platinum group metal that can be used for this conversion, as well as to the method of preparation thereof.

PRIOR ART

Numerous patents describe the addition of promoters to platinum-based catalysts in order to improve their performance with regard to the reforming of hydrocarbon feedstocks. In this respect, patent US 2,814,599 describes the addition of promoters such as gallium, indium, scandium, yttrium, lanthanum, thallium or actinium to platinum- or palladium-based catalysts.

Patent US 4,522,935 describes reforming catalysts comprising platinum, tin, indium and a halogenated compound deposited on a support in which the indium/platinum atomic ratio is greater than 1.14.

Patents US 4,964,975, US 6,600,082 B2 and US 6,605,566 B2 describe catalysts that are based on platinum and tin and can be used in reforming or dehydrogenation processes.

Patent FR 2 840 548 describes a catalyst in the form of a homogeneous bed of particles comprising an amorphous matrix, at least one noble metal, at least one halogen and at least one additional metal. This additional metal is preferentially chosen from the group consisting of tin, germanium, lead, gallium, indium, thallium, rhenium, manganese, chromium, molybdenum and tungsten.

Patent FR2091114 describes a catalyst comprising a group VIII metal, notably platinum, at least one promoter X1 selected from the group consisting of tin and germanium, a halogen compound, and a porous support. The publication F.M. Dautzenberg et al. ("Conversion of n-hexane over Monofunctional Catalysis Supported and Unsupported PtSn Catalysis", Journal of Catalysis, vol 63, 1980, pages 119-128) describes alumina catalysts impregnated with tin and/or platinum, but devoid of halogen.

The publication AKOS FURCHT et al. ("n-Octane reforming over modified catalysis I. The role of Sn, Te and Bi under industrial conditions", Applied Catalysis A: General, vol 226, 2002, pages 155-161) describes catalysts that are based on alumina and comprise tin and platinum. It focuses on the respective effects of Sn, Te and Bi on the properties of the catalyst.

Patent EP0183861 describes a catalyst comprising the combination of the following metals: a platinum group metal, tin, indium and an alkali metal or an alkaline-earth metal. It envisages the optional addition of halogen.

SUMMARY OF THE INVENTION

The present invention relates to the field of bimetallic or multi-metallic catalysts that are based on a noble metal and can be used in a catalytic reforming process.

The invention is defined in Claims 1, 16 and 22 and their dependent claims.

The invention relates to a catalyst comprising a platinum group metal M, at least one promoter X1 selected from the group consisting of tin, germanium and lead, and optionally at least one promoter X2 selected from the group consisting of gallium, indium and thallium, a halogenated compound and a porous support, in which the X1/M, and optionally X2/M, atomic ratio is between 0.3 and 8, the H_{ir}/M ratio measured by hydrogen adsorption is greater than 0.40 and the bimetallicity index BMI measured by hydrogen/oxygen titration is greater than 108.

It has indeed been discovered that the thus defined catalysts lead to improved catalytic performance. The invention also relates to the method for preparing this catalyst and to the process for catalytic reforming in the presence of these catalysts.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a catalyst comprising a platinum group metal M, at least one promoter X1 selected from the group consisting of tin, germanium and lead, a halogenated compound and a porous support, in which the X1/M atomic ratio is between 0.3 and 8.

Preferably, the X1/M ratio is between 0.7 and 5, more preferably between 0.8 and 4, even more preferably between 1.0 and 3.0 and very preferably between 1.0 and 2.9, or even between 1.2 and 2.6.

The catalyst according to the invention may also optionally comprise at least one promoter X2 selected from the group consisting of gallium, indium and thallium. Preferably, the X2/M ratio is then between 0.5 and 6, more preferably said ratio is between 0.8 and 5, even more preferably said ratio is between 0.9 and 4 and very preferably between 1.1 and 4, or even between 1.1 and 3.5.

The catalyst according to the invention preferentially contains 0.01% to 5% by weight of platinum group metal M, more preferably 0.01% to 2% by weight of metal M and even more preferably 0.1% to 1% by weight of metal M. Preferably, the metal M is platinum or palladium and very preferably platinum.

The content of promoter X1 or X2 is preferably between 0.005% and 10% by weight, more preferably between 0.01% and 5% by weight and very preferably between 0.1% and 2% by weight.

Preferably, the promoter X1 is selected from tin and germanium. Preferably, the promoter X2 is indium. The catalyst according to the invention may optionally comprise two promoters such as, for example, tin and indium or germanium and indium. Very preferably, in this case it is tin and indium. According to one variant, the catalyst according to the invention may therefore comprise only a promoter X1, and preferably X1 is tin.

According to another variant, the catalyst according to the invention may comprise both a promoter X1 and a promoter X2, and preferably X1 is tin and X2 is indium.

When the catalyst comprises both at least one promoter X1 and at least one promoter X2, the (X1+X2)/M atomic ratio is preferably between 0.3 and 8, more preferably between 0.8 and 7, even more preferably between 1.4 and 7, very preferably between 1.4 and 6.0, or even between 2.0 and 5.5.

The catalyst may optionally further comprise phosphorus. Catalysts that are preferred according to the invention may therefore comprise for example tin and phosphorus, or tin and gallium and phosphorus, or else tin and indium and phosphorus. Very preferably, in this case it is tin and phosphorus. When the catalyst contains phosphorus, the phosphorus content is preferably between 0.01% and 5% by weight and more preferably between 0.05% and 2% by weight, or even between 0.05% and 1% by weight. When the catalyst according to the invention contains tin, the tin content is preferentially between 0.1% and 2% by weight, and very preferentially between 0.1% and 0.7% by weight, or even between 0.1% and 0.5% by weight.

When the catalyst according to the invention contains indium in a mixture with other promoters X1 or X2 such as, for example, tin or gallium, the indium content is preferably between 0.05%

and 3% by weight, more preferably between 0.1% and 2% by weight and even more preferably between 0.2% and 2% by weight, or even between 0.25% and 1% by weight. The halogenated compound (or the halogen) is preferably selected from the group consisting of: fluorine, chlorine, bromine and iodine. The catalyst contains 0.1% to 15% by weight of halogen, more preferably 0.2% to 8% by weight, even more preferably from 0.5% to 5% by weight. Chlorine is the very preferred halogen and in this case, the catalyst according to the invention contains very preferably 0.5% to 2% by weight, or even 0.7% to 1.5% by weight, of chlorine.

Furthermore, the catalyst according to the invention has a hydrogen adsorption capacity such that the ratio between the amount of irreversibly adsorbed hydrogen and the platinum group metal (also called H_{ir}/M atomic ratio) is greater than 0.40, preferably greater than 0.43, more preferably between 0.43 and 0.9, even more preferably between 0.45 and 0.8, and very preferably between 0.45 and 0.65.

Measurement of the H_{ir}/M ratio

The H_{ir}/M ratio of a catalyst according to the invention is determined by means of the hydrogen chemisorption technique. This technique is known to those skilled in the art and described for example in chapter 5, page 127ff. of the journal book entitled: "Catalytic Naphtha Reforming, Science and Technology" by G.J. Antos, A.M. Aitani and J.M. Parera, published by Marcel Dekker, 1995. Specifically, it enables the characterization of complex systems based on platinum or other metals and on one or more promoters.

Various protocols have been proposed in the literature to determine the amounts of chemisorbed hydrogen. Hydrogen can be reversibly or irreversibly chemisorbed by a metal catalyst. The protocol detailed below is preferred for the determination of the H_{ir}/M ratio according to the invention, which involves the amount H_{ir} of irreversibly chemisorbed hydrogen.

Treatment protocol for the sample:

a) Calcination under a stream of dry air for 2 h at 500°C.

b) Passage into air at ambient temperature for loading into the volumetric measuring cell in less than 10 minutes.

c) Reduction in the cell with increase of the temperature from 20°C to 450°C in 1 h, holding at 450°C for 4 h under a stream of hydrogen (50 mlitres.min^{-1}), return to 25°C under hydrogen, then sealing of the vent of the cell.

Adsorption measurements:

The apparatus used is a static volumetric apparatus.

a) Desorption under dynamic vacuum (10^{-5} mbar, or 1 mPa) at 350°C, 3 h then return to 25°C under vacuum.

b) Measurement of the amount of hydrogen adsorbed at 25°C under a given hydrogen pressure, after adsorption for 60 minutes.

Phases a) and b) are repeated so as to plot the adsorption isotherm between about 40 and 300 mbar (4 to 30 kPa).

Two measurements are carried out by desorbing under vacuum at 25°C for 3 h, which make it possible to measure the amount of hydrogen reversibly adsorbed.

Figure 1 shows an example of an isotherm obtained for a catalyst according to the invention. The bottom curve corresponds to the reversible adsorption isotherm and the top curve represents the total adsorption isotherm.

It is possible to model the adsorption isotherm, assuming dissociative adsorption of hydrogen on platinum, according to the Langmuir equation, with an irreversible part H_{ir} at 25°C and a reversible part H_{rev}.

The total amount of hydrogen adsorbed is defined by equation (I) below:

$$Q_{ads} = H_{ir} + H_{rev.}(K_1.P)^{0.5}/(1+(K_1.P)^{0.5}) \qquad (I)$$

where P is the pressure expressed in mbar (or hectopascal) and K_1 is the Langmuir constant. Modelling the adsorption isotherm therefore makes it possible to determine the parameter H_{ir}.

Bimetallicity index:

The optimized catalyst according to the invention has a bimetallicity index (BMI) of greater than 108. This index, defined below, is measured by the hydrogen/oxygen titration technique. Preferably, this BMI index is greater than 110 and very preferably greater than 115, or even than 120. Furthermore, according to a very preferred variant, this index is less than 170, and even more preferably less than 160, or even less than 150. It is furthermore possible, according to another preferred variant, for this index to be between 108 and 160, or very preferably between 110 and 160, or even between 110 and 150, or else between 115 and 145.

The bimetallicity index (BMI) is determined by exploiting the hydrogen-oxygen titration technique in a particular manner. This technique is known to those skilled in the art for determining the dispersion of a metal, i.e. the ratio of the number of surface atoms of a metal with respect to the total number of atoms of this same metal. It is described for example in chapter 5, pages 130 and 131 of the journal book entitled: "Catalytic Naphtha Reforming, Science and Technology", by G.J. Antos, A.M. Aitani and J.M. Parera, published by Marcel Dekker, 1995. It involves chemisorbing oxygen on a metal M contained in a catalyst that has been previously reduced and therefore contains a layer of chemisorbed hydrogen. The stoichiometric reaction representing the step of titration of the chemisorbed hydrogen by oxygen is considered to be the following:

$$M\text{-}H + 3/4\ O_2 \rightarrow M\text{-}O + \frac{1}{2}\ H_2O$$

The amount of oxygen consumed during the titration makes it possible to determine the amount of accessible metal sites. In the case of a supported bimetallic Pt-Sn system, it has been shown, for example by Sharma et al in Applied Catalysis A 168 (1998) 251, that when performing two successive cycles of oxygen titration, the amount of oxygen adsorbed during the first cycle was greater than that adsorbed during the second cycle. This is explained by the fact that during the first cycle, the reduction of tin contributes to the oxygen consumption, whereas the second cycle essentially reflects the chemisorption of oxygen on the accessible platinum sites.

This second cycle can be used to determine the dispersion of the metal M. In the catalyst according to the invention, the dispersion of the metal M is preferably greater than 80%, more preferably greater than 90% and very preferably greater than 95%.

The bimetallicity index called "BMI" that is used as a criterion in the present invention is calculated from the volume of oxygen consumed during the first hydrogen-oxygen titration. It is calculated as follows:

$$BMI = (V1 /24041) * 4/3 / (0.01\ T_M / MM)$$

with

V1: volume of oxygen consumed during the first titration at 20°C on the previously reduced catalyst, expressed in cm^3 per gram of catalyst

T_M: content of platinum group metal in the catalyst, expressed in % weight

MM: molar mass of the platinum group metal

The bimetallicity index reflects the degree of interaction of the platinum group metal with any promoter present on the catalyst. The preferred hydrogen-oxygen titration experimental protocol to determine the bimetallicity index is the following:

a) calcination of 2 grams of catalyst under a stream of dry air (20 ml/minute) with a flow rate of 1 NI/(g.h) for 2 h at 500°C,

b) return to 20°C under dry air,

c) purge with an inert gas (20 ml/minute), preferably helium with a purity of greater than 99.999%,

d) passage under hydrogen (20 ml/minute), preferably with a purity of greater than 99.999%, and reduction at 500°C for 2 h,
e) return to 20°C,
f) purge with an inert gas (20 ml/minute), preferably helium with a purity of greater than 99.999%,
g) pulses of oxygen with a volume of 0.27 cm^3, preferably with a purity of greater than 99.995% and purified by means of one or more molecular sieves (3A, 4A or 13X sieve), at 20°C until no more oxygen is consumed, or after at least 10 pulses of constant surface area.

The volume of oxygen consumed during step g) is used for the calculation of the bimetallicity index.

Support of the catalyst according to the invention:

The porous support used in the catalyst according to the invention is generally a refractory oxide selected from magnesium oxide, titanium oxide, zirconium oxide, aluminium oxide, silicon oxide, or the mixture thereof. Preferably, it is silica, alumina or silica-alumina, and very preferably alumina.

According to the invention, said porous support is advantageously in the form of beads, extrudates, pellets or powder. Very advantageously, said support is in the form of beads or extrudates. The pore volume of the support is preferably between 0.1 and 1.5 cm^3/g, more preferably between 0.4 and 0.8 cm^3/g. Furthermore, said porous support has a specific surface area of advantageously between 50 and 600 m^2/g, preferably between 100 and 400 m^2/g, or even between 150 and 300 m^2/g.

Preparation of the catalyst according to the invention:

It has been discovered by the applicant that the catalysts according to the invention were obtained in particular by depositing the promoter X1 in two stages (two distinct steps), a first step that takes place before the introduction of the platinum group element, and a second step that takes place after the introduction of the platinum group element.

The process for preparing the catalyst according to the invention generally comprises the following steps:

a) introduction of the promoter X1 into the support or onto the support,

b) optional step of drying of the product obtained on conclusion of step a,

c) calcination of the product obtained in step a or optionally in step b at a temperature preferably of between 350°C and 650°C,

d) deposition of at least one platinum group metal M,

e) optional drying under an atmosphere that is neutral or contains oxygen, at a moderate temperature that preferably does not exceed 150°C,

f) deposition of a complementary fraction of the promoter X1 on the product obtained in step d or e, said complementary fraction of said promoter X1 being deposited by contacting of a tin tetrachloride or germanium tetrachloride solution,

g) optional drying of the product obtained in step f,

h) calcination of the product obtained in step f or g; this calcination is preferably carried out in the presence of air and this air may also be enriched in oxygen or in nitrogen, and in the case where the precursors of the promoter X1 or of the metal M that are used in the preparation of the catalyst do not contain halogen or contain an insufficient amount of halogen, addition of a halogenated compound during the preparation or, when the halogen is chlorine, an oxychlorination treatment or impregnation with an aqueous hydrochloric acid solution.

More precisely, for the first step (step a) of introduction of the promoter X1 (used alone or in a mixture), X1 may be incorporated into the support, for example during the synthesis of the support or during the forming of the support. X1 may also be introduced onto the support, for example by impregnation of the preformed support. X1 may also be introduced partly during the synthesis or forming of the support and partly by deposition onto the formed support. 30% to 70% by weight, preferably 40%

to 65% by weight and even more preferably 50% to 65% by weight, of the total amount of X1 entering into the composition of the catalyst according to the invention is thus introduced into the support or deposited onto the support during this first introduction step.

The fraction of X1 introduced during the synthesis of the support is incorporated by any technique known to those skilled in the art. Without being exhaustive, the techniques for addition before or during the dissolution of the oxide precursors of the support, with or without maturation, may be suitable. The introduction may therefore be simultaneous with or subsequent to the mixing of the precursors of the support.

According to a variant of the preparation method according to the invention, the promoter X1 is introduced during the synthesis of the support according to a sol-gel technique. According to another variant, the promoter X1 is added to an alumina sol.

According to a third implementation variant of the invention, the promoter X1 is introduced during the forming of the support according to the techniques of the prior art for forming the support, such as the procedures for forming by extrusion or by oil-drop.

In the case where the fraction of X1 is deposited onto the support, after its forming, it may be impregnated by means of any technique known to those skilled in the art, and preferably by impregnation of a solution containing one or more precursors of X1. The impregnation may be performed by an excess of solution or else dry impregnation (the volume of solution containing X1 corresponding to the pore volume of the support). The impregnation may be performed in the presence of species acting on the interaction between the precursor of the promoter X1 and the support. These species may be, for example, and without being limiting, mineral acids (HCl, HNO_3) or organic acids (such as carboxylic or polycarboxylic acids), and organic compounds of complexing type, as described, for example, in patents US 6,872,300 B1 and US 6,291,394 B1. Preferably, the impregnation is performed according to any technique known to those skilled in the art making it possible to obtain a uniform distribution of the promoter X1 within the catalyst.

The precursors of the promoter X1 may be mineral or of organometallic type, optionally of water-soluble organometallic type. X1 is preferably chosen from the elements germanium and tin. The precursors containing germanium may be chosen from at least one of the following reactants, without being exhaustive: oxides, tetraalkoxides and fluorides of germanium. An example of an organosoluble organometallic compound is the oxide $(EtGeO)_2O$. In the case of tin, various precursors may be used, alone or in a mixture. In particular, the tin may be chosen, and this in a non-limiting manner, from the group formed by halogenated compounds, hydroxides, carbonates, carboxylates, sulfates, tartrates and nitrates. These forms of tin may be introduced into the medium for preparing the catalyst as they are, or generated in situ (for example by introduction of tin and carboxylic acid). The precursors of tin-based organometallic type may be, for example, SnR_4, where R represents an alkyl group, for example the butyl group, Me_3SnCl, Me_2SnCl_2, Et_3SnCl, Et_2SnCl_2, $EtSnCl_3$, $iPrSnCl_2$ and the hydroxides Me_3SnOH, $Me_2Sn(OH)_2$, EtsSnOH, $Et_2Sn(OH)_2$, the oxides $(Bu_3Sn)_2O$, and the acetate $Bu_3SnOC(O)Me$. Preferably, halogenated tin species, in particular chlorinated tin species, will be used. In particular, $SnCl_2$ or $SnCl_4$ will advantageously be used.

Regardless of the variant used for the introduction of a fraction of the promoter X1 during step a, it may be preferred to perform drying of the support (step b) at the end after addition of the promoter. This drying may be performed according to any technique known to those skilled in the art, for example at a temperature of between 40°C and 200°C, preferably between 80°C and 180°C. This drying may be performed with temperature programming and may optionally comprise stationary temperature phases.

Since the promoter X1 has been introduced into the support or onto the previously formed support, the protocol for preparing the catalysts according to the invention generally requires a calcination before the deposition of the platinum group metal M (step c). This calcination is preferably carried out at a temperature of between 350°C and 650°C and preferably of between 400°C and 600°C and even more preferably of between 400°C and 550°C. The temperature increase may be regular or may include intermediate stationary temperature phases, these stationary phases being reached with fixed or variable rates of temperature increase. These temperature increases may therefore be identical or may differ in their rate (in degrees per minute or per hour). The gas atmosphere used during the calcination contains oxygen, preferably between 2% and 50% and more preferably between 5% and 25%. Air may therefore also be used during this calcination step.

After obtaining the support containing a fraction of X1 relative to the final composition of the catalyst, platinum group metal M is deposited (step d). In this step, the metal M may be introduced by dry impregnation or impregnation with an excess of solution, using a precursor or a mixture of precursors containing a platinum group metal M. The impregnation may be performed in the presence of species acting on the interaction between the precursor of the metal M and the support. These species may be, and without being limiting, mineral acids (HCl, HNO_3) or organic acids (such as carboxylic or polycarboxylic acids), and organic compounds of complexing type. Preferably, the impregnation is performed according to any technique known to those skilled in the art making it possible to obtain a uniform distribution of the metal M within the catalyst.

The precursors of the metal M form part of the following group, without this list being limiting: hexachloroplatinic acid, bromoplatinic acid, ammonium chloroplatinate, platinum chlorides, dichlorocarbonylplatinum dichloride, tetraammineplatinum chloride.

At this stage, the support containing X1 (a fraction of the total amount of X1 aimed for in the final catalyst) and the platinum is optionally dried (step e), under an atmosphere that is neutral or contains oxygen (it being possible to use air), at a temperature that is moderate and preferably does not exceed 150°C. Preferably, the drying is carried out at a temperature less than 100°C and over a period of a few minutes to a few hours.

On conclusion of this optional drying step, a complementary fraction of the promoter X1 is deposited onto the product obtained in step d or e (step f). More precisely, for the introduction of the species X1 (used alone or in a mixture) with respect to this step, at least 30% and at most 70%, preferably at least 35% and at most 60%, and very preferably at least 35% and at most 50%, of the total amount of X1 entering into the composition of the catalyst according to the invention is thus introduced during this second step (step f) of introduction of X1. The complementary fraction of the promoter X1 is deposited by contacting with a solution containing the precursor.

In this step, and in the case of precursors of tin, tin tetrachloride $SnCl_4$ will be exclusively used. In the case of precursors of germanium, germanium tetrachloride $GeCl_4$ will be exclusively used.

The product obtained in step f may then be optionally dried (step g), under an atmosphere that is neutral or contains oxygen (it being possible to use air), at a moderate temperature.

This step is then generally followed by a calcination of the product obtained in step f or g (step h). This calcination is preferably carried out in the presence of air. This air may also be enriched in oxygen or in nitrogen. Preferably, the oxygen content of this gas ranges from 0.5% to 30% and even more preferably 2% to 25%.

This calcination is carried out at a temperature of between 350°C and 600°C and preferably between 400°C and 550°C and even more preferably between 450°C and 550°C. The temperature ramp must be regular and sufficiently rapid. It may optionally contain stationary temperature phases from 350°C. The temperature increase rate will be greater than or equal to 5°C/min. This temperature increase rate may be greater than 10°C/min. Preferably, this temperature increase rate will not be less than 2°C/min.

The optional promoter X2 may be introduced in one or more steps of the preparation of the catalyst. For example, it may be introduced before, during or after the first step of introduction of X1 (step a, during the forming of the support or by deposition onto the support), alone or in a mixture. X2 may also be introduced between the step of calcination of the support (step c) and the step of introduction of the platinum group metal (step d). Another possibility for the introduction of X2 is to incorporate it before the addition of the second fraction of X1 (step f); it may lastly be introduced before the final calcination step (step h). The promoter X2 may be introduced in one or more stages, provided that the above-mentioned conditions of introduction are respected. The promoter X2 may also be introduced by impregnation during an additional step (step i) that takes place after step h; step i is then generally followed by steps j and k respectively of drying and of calcination of the catalyst under the conditions detailed previously for the drying steps e or g or calcination step h.

In the case where a promoter X2 is present, the preparation process according to the invention may therefore further and advantageously comprise an additional step of introduction of a promoter X2 that takes place before step a, or between step c and step d or just before step f or step h, or even after step h.

The optional promoter X2 may be introduced by means of any technique known to those skilled in the art. Ionic exchanges, dry impregnations or impregnations with an excess of solution are appropriate for the deposition onto the support (modified or unmodified by X1). In the case of incorporation during the preparation of the support, the promoter X2 may be added by mixing, co-precipitation, dissolution, without being limiting. In the case of gallium, indium, and thallium, use may be made of nitrates or halides. With respect to indium, precursors, alone or in a mixture, of indium nitrate, chlorides or bromides are suitable. Other precursors may also be used.

When the various precursors used in the preparation of the catalyst according to the invention do not contain halogen or contain an insufficient amount of halogen, it may be necessary to add a halogenated compound during the preparation. Any compound known to those skilled in the art may be used and incorporated in any one of the steps of the preparation of the catalyst according to the invention. In particular, it is possible to use compounds of Friedel-Crafts type such as aluminium chloride or bromide, iron chloride or bromide or zinc chloride. It is also possible to use organic compounds such as methyl or ethyl halides, for example dichloromethane, chloroform, dichloroethane, methylchloroform or carbon tetrachloride.

The chlorine may also be added to the catalyst according to the invention by means of an oxychlorination treatment. Such a treatment may for example be carried out at 500°C for 4 hours under a flow of 100 litres per hour of air containing the amount of chlorine gas necessary to deposit the desired amount of chlorine and an amount of water with a H_2O/Cl molar ratio close for example to 20.

The chlorine may also be added by means of impregnation with an aqueous hydrochloric acid solution. A typical protocol involves impregnating the solid so as to introduce the desired amount of chlorine. The catalyst is kept in contact with the aqueous solution for a period that is long enough to deposit this amount of chlorine, and then the catalyst is drained and dried at a temperature of between 80°C and 150°C, and then finally calcined under air at a temperature of between 450°C and 600°C.

The invention also relates to a process for the catalytic reforming of a hydrocarbon feedstock in the presence of the catalyst according to the invention.

The catalyst according to the invention may indeed be used in processes for reforming gasolines and for producing aromatic compounds.

The reforming processes make it possible to increase the octane number of the gasoline fractions originating from the distillation of crude oil and/or from other refining processes, for instance catalytic cracking or thermal cracking. The processes for producing aromatics provide the base products (benzene, toluene, xylenes) that can be used in the petrochemical industry. These processes have an additional benefit, contributing to the production of large amounts of hydrogen, essential for refinery hydrotreating and hydroconversion processes. These two types of processes differ by the choice of operating conditions and the composition of the feedstock, which are known to those skilled in the art.

The feedstock for the reforming processes generally contains paraffinic, naphthenic and aromatic hydrocarbons containing from 5 to 12 carbon atoms per molecule. This feedstock is defined, inter alia, by its density and its composition by weight. These feedstocks may have an initial boiling point of between 40°C and 70°C and a final boiling point of between 160°C and 220°C. They may also be formed by a gasoline fraction or a mixture of gasoline fractions having initial and final boiling points of between 40°C and 220°C. The feedstock may thus also be formed by a heavy naphtha having a boiling point of between 160°C and 200°C.

Typically, the reforming catalyst is loaded into a unit and subjected first to a reduction treatment. This reduction step is generally carried out under a dilute or pure hydrogen atmosphere and at a temperature advantageously of between 400°C and 600°C, preferably between 450°C and 550°C.

The feedstock is then introduced in the presence of hydrogen and with a hydrogen/hydrocarbons of the feedstock molar ratio generally of between 0.1 and 10, preferably between 1 and 8. The operating conditions of the reforming are generally the following: a temperature preferably of between 400°C and 600°C, more preferably between 450°C and 540°C, and a pressure preferably of between 0.1 MPa and 4 MPa and more preferably between 0.25 MPa and 3.0 MPa. All or some of the hydrogen produced may be recycled to the inlet of the reforming reactor.

EXAMPLES:

The examples that follow illustrate the invention.

Example 1 (invention): *Preparation of catalyst A SnPtSn/Al2O3-Cl*

A catalyst A is prepared containing 0.3% by weight of platinum, 0.4% by weight of tin, and 1% by weight of chlorine, deposited on a gamma alumina support having a specific surface area of 200 m^2/g.

200 cm^3 of an aqueous solution containing tin dichloride in the presence of hydrochloric acid is added to 100 g of alumina support. The support is left in contact with the solution for 4 hours, filtered, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour. The amount of tin dichloride is chosen so as to obtain 0.2% by weight of tin on the calcined product. The solid is then brought into contact with 400 cm^3 of an aqueous solution of hexachloroplatinic acid and of hydrochloric acid. The solid is left in contact with the solution for 4 hours and then drained. It is dried at 90°C and then brought into contact with 200 cm^3 of an aqueous solution containing tin tetrachloride in the presence of hydrochloric

acid. It is left in contact with the solution for 4 hours, filtered, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour, with a temperature increase rate of 7°C per minute. The amount of tin tetrachloride is chosen so as to obtain a total of 0.4% by weight of tin on the calcined product.

<u>Example 2</u> (invention): ***Preparation of catalyst B SnPtSn/Al2O3-Cl***

A catalyst B is prepared according to the procedure described in Example 1, this time choosing the amount of tin dichloride so as to obtain 0.27% by weight of tin on the calcined intermediate product, and the amount of tin tetrachloride so as to complete to always obtain 0.4% of tin on the final catalyst.

<u>Example 3</u> (comparative): ***Preparation of catalyst C SnPt/Al2O3-Cl***

A catalyst C is prepared on the same support and with the same contents of tin, platinum and chlorine as in Example 1.

200 cm^3 of an aqueous solution containing tin dichloride in the presence of hydrochloric acid is added to 100 g of alumina support. The support is left in contact with the solution for 4 hours, filtered, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour. The amount of tin dichloride is chosen so as to obtain 0.4% by weight of tin on the calcined product. The solid is then brought into contact with 400 cm^3 of an aqueous solution of hexachloroplatinic acid and of hydrochloric acid. The solid is left in contact with the solution for 4 hours and then drained. It is dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour, with a temperature increase rate of 7°C per minute.

<u>Example 4</u> (comparative): ***Preparation of a catalyst D SnPtSn/Al2O3-Cl***

A catalyst C is prepared according to the procedure described in Example 1, with the only difference that, during the two tin impregnations, the precursor used is filtered, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour. The amount of tin dichloride is chosen so as to obtain 0.4% by weight of tin on the calcined product. The solid is then brought into contact with 400 cm^3 of an aqueous solution of hexachloroplatinic acid and of hydrochloric acid. The solid is left in contact with the solution for 4 hours and then drained. It is dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour, with a temperature increase rate of 7°C per minute.

Example 4 (comparative): ***Preparation of a catalyst D SnPtSn/Al2O3-Cl***

A **catalyst D** is prepared according to the procedure described in Example 1, with the only difference that, during the two tin impregnations, the precursor used is an aqueous solution containing tin dichloride in the presence of hydrochloric acid.

Example 5 (invention): ***Preparation of catalyst E SnPtInSn/Al2O3-Cl***

A catalyst E is prepared on the same support as in Example 1, by depositing 0.3% by weight of platinum, 0.4% by weight of tin, 0.2% by weight of indium and 1% by weight of chlorine. 200 cm^3 of an aqueous solution containing tin dichloride in the presence of hydrochloric acid is added to 100 g of alumina support. The support is left in contact with the solution for 4 hours, filtered, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour. The amount of tin dichloride is chosen so as to obtain 0.2% by weight of tin on the calcined product. The solid is then brought into contact with 400 cm^3 of an aqueous solution of hexachloroplatinic acid and of hydrochloric acid. The solid is left in contact with the solution for 4 hours and then drained. It is dried at 90°C and then brought into contact with 300 cm^3 of an aqueous solution containing indium nitrate in the presence of hydrochloric acid. It is once again left in contact with the solution for 4 hours, drained, dried and then brought into contact with 200 cm^3 of an aqueous solution containing tin tetrachloride in the presence of hydrochloric acid. It is left in contact with the solution for 4 hours, drained, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour, with a temperature increase rate of 7°C per minute. The amount of is an aqueous solution containing tin dichloride in the presence of hydrochloric acid.

Example 5 **(invention):** ***Preparation of catalyst E SnPtInSn/Al2O3-Cl***

A catalyst E is prepared on the same support as in Example 1, by depositing 0.3% by weight of platinum, 0.4% by weight of tin, 0.2% by weight of indium and 1% by weight of chlorine. 200 cm^3 of an aqueous solution containing tin dichloride in the presence of hydrochloric acid is added to 100 g of alumina support. The support is left in contact with the solution for 4 hours, filtered, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour. The amount of tin dichloride is chosen so as to obtain 0.2% by weight of tin on the calcined product. The solid is then brought into contact with 400 cm^3 of an aqueous solution of hexachloroplatinic acid and of hydrochloric acid. The solid is left in contact with the solution for 4 hours and then drained. It is dried at 90°C and then brought into contact with 300 cm^3 of an aqueous solution containing indium nitrate in the presence of hydrochloric acid. It is once again left in contact with the solution for 4 hours, drained, dried and then brought into contact with 200 cm^3 of an aqueous solution containing tin tetrachloride in the presence of hydrochloric acid. It is left in contact with the solution for 4 hours, drained, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour, with a temperature increase rate of 7°C per minute. The amount of tin tetrachloride is chosen so as to obtain a total of 0.4% by weight of tin on the calcined product.

<u>Example 6</u> (invention): ***Preparation of catalyst F PtSn/(Al2O3-Sn-In)-Cl***

A support of alumina beads, containing 0.2% by weight of tin and 0.2% by weight of indium, with an average diameter of 1.2 mm, having a BET surface area of 205 m^2/g, is prepared by bringing tin dichloride and indium trichloride into contact with an alumina hydrosol obtained by hydrolysis of aluminium chloride. The alumina hydrosol thus obtained is then passed through a vertical column filled with additivated oil. The spheres thus obtained are heat-treated up to 600°C so as to obtain beads with good mechanical strength.

A catalyst F is prepared on this support, by depositing 0.3% by weight of platinum, an additional 0.2% by weight of tin so as to obtain 0.4% by weight of tin, and 1% by weight of chlorine on the final catalyst.

400 cm^3 of an aqueous solution of hexachloroplatinic acid and of hydrochloric acid are added to 100 g of the alumina support containing tin and indium. The solid is left in contact with the solution for 4 hours and then drained. It is dried at 90°C and then brought into contact with 200 cm^3 of an aqueous solution of tin tetrachloride in the presence of hydrochloric acid. It is left in contact with the solution for 4 hours, drained, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour, with a temperature increase rate of 7°C per minute. The amount of tin tetrachloride is chosen so as to obtain a total of 0.4% by weight of tin on the calcined product.

<u>Example 7</u> (invention): ***Preparation of catalyst G SnInPtSn/Al2O3***

A catalyst G is prepared on the same support as in Example 1, by depositing 0.3% by weight of platinum, 0.4% by weight of tin, 0.2% by weight of indium and 1% by weight of chlorine. 200 cm^3 of an aqueous solution containing tin dichloride in the presence of hydrochloric acid is added to 100 g of alumina support. The support is left in contact with the solution for 4 hours, filtered, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour. The amount of tin dichloride is chosen so as to obtain 0.2% by weight of tin on the calcined product. The solid is then brought into contact with 300 cm^3 of an aqueous solution containing indium nitrate in the presence of hydrochloric acid. The solid is once again left in contact with the solution for 4 hours, drained and dried. The solid is then brought into contact with 400 cm^3 of an aqueous solution of hexachloroplatinic acid and of hydrochloric acid. The solid is left in contact with the solution for 4 hours and then drained. It is dried at 90°C and then brought into contact with 200 cm^3 of an aqueous solution containing tin tetrachloride in the presence of hydrochloric acid. It is left in contact with the solution for 4 hours, drained, dried at 120°C and then calcined for 2 hours at 500°C under a flow of air of 100 litres per hour, with a temperature increase rate of 7°C per minute. The amount of tin tetrachloride is chosen so as to obtain a total of 0.4% by weight of tin on the calcined product.

***Example 8*: Evaluation of the performance of catalysts A to G in catalytic reforming**

The values for the bimetallicity index and the H_{ir}/Pt atomic ratio of catalysts A to G of Examples 1 to 7 were determined according to the methods presented in the detailed description and are indicated in Table 1.

Samples of the catalysts of which the preparations have been described in Examples 1 to 7 were used in a reaction bed suitable for the conversion of a hydrocarbon feedstock, of naphtha type obtained from oil distillation. This naphtha has the following composition (by mass):
40.5% of paraffinic compounds,
45.1% of naphthenes,

14.4% of aromatic molecules,
for a total density of 0.757 g/cm³.

The research octane number of the feedstock is close to 55.

After loading into the reactor, the catalysts are activated by heat treatment under a pure hydrogen atmosphere, for a period of 2 hours at 490°C.

Table 1: features and performance of catalysts A to G

Catalyst	BMI (%)	H_{Ir}/Pt	Yield of reformate (% by weight)	Research octane number RON	Yield of aromatics (% by weight)	Yield of C1-C4 (% by weight)
A (invention)	115	0.52	+0.45%	101.9	+0.2	-0.3
B (invention)	111	0.55	Base	102.3	Base	Base
C (prior art)	103	0.65	-0.95	101.9	-0.85%	+1.1
D (prior art)	109	0.34	-0.85%	101.9	-0.9%	+0.75%
E (invention)	130	0.50	+1.4%	102.0	+1.25%	-1.50%
F (invention)	122	0.51	+1.3%	101.9	+1.1%	-1.4%
G (invention)	133	0.49	+1.7%	102.2	+1.4%	-1.8

The evaluation of the catalytic performance is performed under reforming reaction conditions, in the presence of hydrogen and the naphtha described previously. In particular, the conditions for the implementation and comparison of the catalysts are the following:

- pressure of the reactor kept at 8 barg (0.8 MPag),

- feedstock flow rate of 2.0 kg/h per kg of catalyst,
- hydrogen/hydrocarbons of the feedstock molar ratio: 4

The comparison is performed at an equivalent quality of research octane number of the liquid effluents (called reformates) resulting from the catalytic conversion of the feedstock. The comparison is performed for a research octane number of 102.

Patentkrav

1. Katalysator, der omfatter et metal M fra platingruppen, mindst en promotor X1, der er valgt fra gruppen bestående af tin, germanium og bly, en halogenforbindelse og en porøs bærer, hvor atomforholdet X1/M er på mellem 0,3 og 8, H_{ir}/M-forholdet, målt ved irreversibel hydrogen-kemisorption er større end 0,40, og IBM-bimetallicitetsindekset, målt ved hydrogen/oxygentitrering, er større end 108, idet katalysatoren indeholder 0,1 til 15 vægt-% halogforbindelse og fremstilles ifølge følgende trin:
a) indføring af promotoren X1 i bæreren eller på bæreren
c) kalcinering af det i trin a) opnåede produkt ved en temperatur, der fortrinsvis ligger mellem 350 og 650 °C
d) aflejring af mindst ét metal fra platingruppen M
e) eventuel tørring i en neutral atmosfære eller i en oxygenholdig atmosfære ved en moderat temperatur, som fortrinsvis ikke overstiger 150 °C
f) aflejring af en komplementær fraktion af promotoren X1 på det i trin d) eller e) opnåede produkt, idet den komplementære fraktion af promotoren X1 aflejres ved kontakt med en opløsning af tintetrachlorid eller germaniumtetrachlorid
h) kalcinering af det i trin f) opnåede produkt, idet denne kalcinering fortrinsvis udføres i nærvær af luft, og denne luft ligeledes kan være beriget med oxygen eller nitrogen
og såfremt forstadierne til den promotor X1 eller det metal M, der anvendes ved fremstillingen af katalysatoren, ikke indeholder halogen eller indeholder halogen i en utilstrækkelig mængde, tilsætning af en halogenforbindelse under fremstillingen eller, når halogenet er chlor, en oxychloreringsbehandling eller en imprægnering med en vandig opløsning af saltsyre.

2. Katalysator ifølge krav 1, der i øvrigt omfatter mindst én promotor X2, der er valgt fra gruppen bestående af gallium, indium og thallium, idet X2/M-forholdet er på mellem 0,3 og 8.

3. Katalysator ifølge et af kravene 1 eller 2, hvor atomforholdet X1/M er på mellem 0,6 og 6.

4. Katalysator ifølge krav 2, hvor atomforholdet (X1+X2)/M er på mellem 0,3 og 8.

5. Katalysator ifølge krav 2, hvor forholdet X1/M er på mellem 1,0 og 2,9, og forholdet X2/M er på mellem 0,9 og 4.

6. Katalysator ifølge krav 1, der kun omfatter en promotor X1, og hvor X1 er tin.

7. Katalysator ifølge krav 2, der omfatter en promotor X1 og en promotor X2, og hvor X1 er tin og X2 er indium.

8. Katalysator ifølge et af de foregående krav, hvor katalysatoren i øvrigt omfatter phosphor.

9. Katalysator ifølge krav 8, hvor phosphorindholdet er på mellem 0,01 og 5 vægt-%.

10. Katalysator ifølge et af de foregående krav, hvor atomforholdet H_{ir}/M er på mellem 0,43 og 0,9.

11. Katalysator ifølge et af de foregående krav, hvor forholdet H_{ir}/M er på mellem 0,45 og 0,65.

12. Katalysator ifølge et af de foregående krav, hvor IBM-bimetallicitetsindekset, målt ved hydrogen/oxygentitrering, er større end 115.

13. Katalysator ifølge et af kravene 1 til 11, hvor IBM-bimetallicitetsindekset, målt ved hydrogen/oxygentitrering, er på mellem 110 og 160, fortrinsvis mellem 115 og 145.

14. Katalysator ifølge et af de foregående krav, hvor halogenforbindelsen er valgt fra gruppen bestående af: fluor, chlor, brom og iod.

15. Katalysator ifølge et af de foregående krav, hvor halogenforbindelse er chlor, og katalysatoren indeholder 0,5 til 2 vægt-% chlor.

16. Fremgangsmåde til fremstilling af en katalysator, der omfatter et metal M fra platingruppen, mindst en promotor X1, der er valgt fra gruppen bestående af tin, germanium og bly, en halogenforbindelse og en porøs bærer, hvor atomforholdet X1/M er på mellem 0,3 og 8, H_{ir}/M-forholdet, målt ved irreversibel hydrogen-kemisorption er større end 0,40, og IBM-bimetallicitetsindekset, målt ved hydrogen/oxygentitrering, er større end 108, idet katalysatoren indeholder 0,1 til 15 vægt-% halogenforbindelse, idet fremgangsmåden omfatter følgende trin:
a) indføring af promotoren X1 i bæreren eller på bæreren
c) kalcinering af det i trin a) opnåede produkt ved en temperatur, der fortrinsvis ligger mellem 350 og 650 °C
d) aflejring af mindst ét metal fra platingruppen M
e) eventuel tørring i en neutral atmosfære eller i en oxygenholdig atmosfære ved en moderat temperatur, som fortrinsvis ikke overstiger 150 °C
f) aflejring af en komplementær fraktion af promotoren X1 på det i trin d) eller e) opnåede produkt, idet den komplementære fraktion af promotoren X1 aflejres ved kontakt med en opløsning af tintetrachlorid eller germaniumtetrachlorid
h) kalcinering af det i trin f) opnåede produkt, idet denne kalcinering fortrinsvis udføres i nærvær af luft, og denne luft ligeledes kan være beriget med oxygen eller nitrogen
og såfremt forstadierne til den promotor X1 eller det metal M, der anvendes ved fremstillingen af katalysatoren, ikke indeholder halogen eller indeholder halogen i en utilstrækkelig mængde, tilsætning af en halogenforbindelse under fremstillingen eller, når halogenet er chlor, en oxychloreringsbehandling eller en imprægnering med en vandig opløsning af saltsyre.

17. Fremgangsmåde til fremstilling ifølge krav 16, der iøvrigt omfatter et trin b) med tørring af det i slutningen af trin a) opnåede produkt.

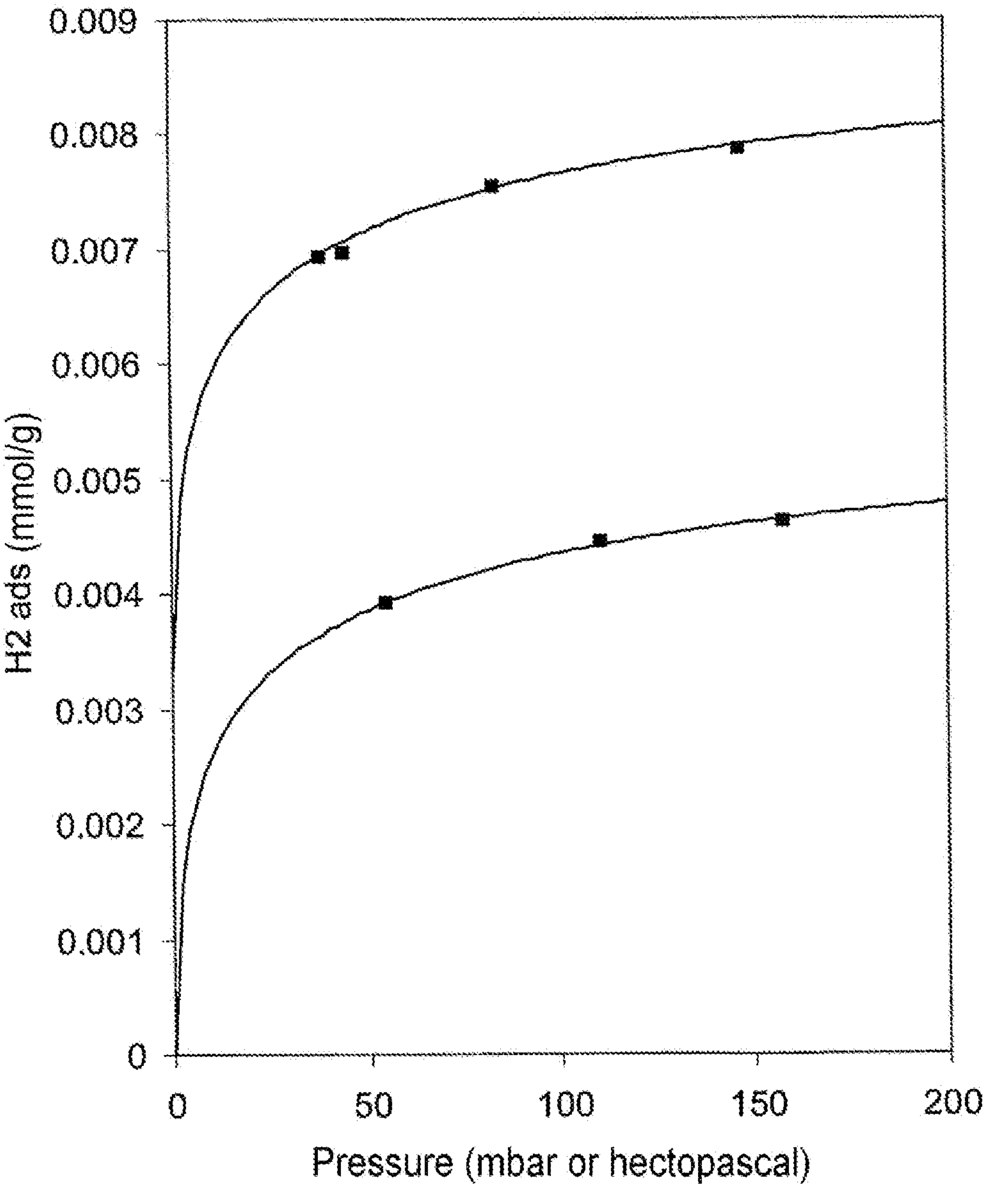
18. Fremgangsmåde til fremstilling ifølge et af kravene 16 eller 17, der i øvrigt forud for trin h) omfatter et trin g) med tørring af det i slutningen af trin f) opnåede produkt.

19. Fremgangsmåde til fremstilling ifølge et af kravene 16 til 18, hvorved en promotor X2 indføres ved ét eller flere trin af fremstillingen, der er valgt blandt trin a), d) og f).

20. Fremgangsmåde til fremstilling ifølge et af kravene 16 til 19, der i øvrigt omfatter et yderligere trin med indføring af en promotor X2, som finder sted forud for trin a), eller mellem trin c) og trin d), eller lige før trin f) eller trin h), eller efter trin h).

21. Fremgangsmåde til fremstilling ifølge et af kravene 16 til 20, hvorved mindst 30 % og højst 70 % af den samlede mængde X1, der indgår i sammensætningen af katalysatoren ifølge opfindelsen, indføres under det andet trin f) til indføring af X1.

22. Fremgangsmåde til katalytisk reforming af et carbonhydridholdigt råmateriale i nærvær af katalysatoren ifølge et af kravene 1 til 15.



0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
H2 ads (mmol/g)
0
50
100
150
200
Pressure (mbar or hectopascal)

Figure 1