Despite recent progress in the field, there is a need for improved materials, in particular porous materials for use in guard beds for removing of impurities such as P, in particular also for feedstocks comprising a significant portion of renewables including a feedstock with 100% renewables, i.e. a 100% renewable feed.

SUMMARY ~~OF THE INVENTION~~

In an aspect of the present disclosure, there is provided a porous material comprising alumina,
- said alumina comprising alpha-alumina,
- said porous material comprising one or more metals selected from Co, Mo, Ni, W, and combinations thereof,
- said porous material having a BET-surface area of 1-110 m^2/g,
wherein
- the porous material has a total pore volume of 0.50-0.80 ml/g, such as 0.50-0.75 ml/g, or 0.55-0.70 ml/g, or 0.60-0.70 ml/g, as measured by mercury intrusion porosimetry, and
- the porous material has a pore size distribution (PSD) with at least 30 vol% of the total pore volume, such as at least 40 vol%, at least 50 vol%, or at least 60 vol% being in pores with a radius ≥ 400 Å suitably in pores with a radius ≥ 500 Å, such as pores with a radius up to 5000 Å.

In another aspect of the present disclosure, there is provided a process for removing one or more impurities from a feedstock, said process comprising the step of contacting said feedstock with a guard bed comprising a porous material disclosed herein, thereby providing a purified feedstock.

In a further aspect of the present disclosure, there is provided a guard bed for a hydrotreatment system, said guard bed comprising a porous material disclosed herein.

In another aspect of the present disclosure, there is provided a hydrotreatment system for hydrotreating a feedstock, said hydrotreatment system comprising:
a guard bed comprising a porous material disclosed herein; and

a hydrotreatment section comprising at least one hydrotreatment catalyst, arranged downstream of said guard bed.

In a further aspect of the present disclosure, there is provided a use of a porous material disclosed herein as a phosphorus guard in a hydrotreatment process.

It is an object of the present ~~invention~~disclosure to provide a material comprising one or more metals with hydrotreating activity that is capable of capturing impurities, particularly P, in hydrocarbon feedstocks, and which minimize coking during operation.

It is another object of the present ~~invention~~disclosure to provide a material with a higher P penetration and thereby improved P-capture than conventional materials.

It is a further object of the present ~~invention~~disclosure to provide a material with high capacity for capturing impurities, particularly P, in a feedstock originating from a renewable source, or a feedstock combining a renewable source and a fossil fuel.

These and other objects are solved by the present ~~invention~~disclosure.

Accordingly, in a first ~~aspect~~example the ~~invention~~disclosure is a porous material, in particular a porous material for removing one or more impurities from a feedstock, comprising alumina,

- said alumina comprising alpha-alumina,
- said porous material comprising one or more metals selected from Co, Mo, Ni, W, and combinations thereof,
- said porous material having a BET-surface area of 1-110 m^2/g,

wherein,

- the porous material has a total pore volume of 0.50-0.80 ml/g, such as 0.50-0.750 ml/g, or 0.55-0.70 ml/g, or 0.60-0.7 ml/g (600-700 ml/kg), as measured by mercury intrusion porosimetry,

and

- the porous material has a pore size distribution (PSD) with at least 30 vol% of the total pore volume, such as at least 40 vol%, at least 50 vol%, or at least 60 vol% being

in pores with a radius ≥ 400 Å (40 nm) suitably in pores with a radius ≥ 500 Å (50 nm), such as pores with a radius up to 5000 Å (500 nm).

In an ~~embodiment~~example according to the first ~~aspect~~example of the ~~invention~~disclosure, up to 60 vol% of the total pore volume, such as up to 40 vol% of the total pore volume is in pores with a radius below 400 Å, such as pores with a radius down to 40 Å, or down to 80 Å.

The mercury intrusion porosimetry is conducted according to ASTM D4284.

While the bigger pores with radius equal to or above 400 Å, or equal to or above 500 Å, serve for the P-capture, the smaller pores with radius below 400 Å enable better use of the one or more metals in the porous material for providing hydrotreating activity. The porous material may for instance show a broad peak as a unimodal pore system or show a bimodal or even trimodal pore system, in which particularly the smaller pores add the possibility for providing the hydrotreating activity to the porous material.

The BET-surface area is measured according to ASTM D4567-19, i.e. single-point determination of surface area by the BET equation.

In an ~~embodiment~~example according to the first ~~aspect~~example of the ~~invention~~disclosure, the content of alpha-alumina is 50-100 wt**%** such as 65-95 wt%, or 60-80 wt%, as determined by XRD.

In an ~~embodiment~~example according to the first ~~aspect~~example of the ~~invention~~disclosure, the alumina further comprises theta-alumina and optionally gamma-alumina.

In an ~~embodiment~~example according to the first ~~aspect~~example of the ~~invention~~disclosure, the content of theta-alumina is 0-50 wt% such as 35-45 wt%, or 30-40 wt%, as determined by XRD.

In an ~~embodiment~~example according to the first ~~aspect~~example of the ~~invention~~disclosure, the content of gamma-alumina is 0-10 wt%, such as 5 wt% or less e.g. 1 wt%, as determined by XRD. Accordingly, in a particular ~~embodiment~~example, the content of gamma-alumina is 0 wt%, i.e. the porous material is free of gamma-alumina.

In an ~~embodiment~~example according to the first ~~aspect~~example of the ~~invention~~disclosure, the content of the one or more metals is 0.25-20 wt%, such as 0.25-15 wt%, 0.25-10 wt%, or 0.25-5 wt%.

A combination of the above features is also encompassed. Accordingly, in an ~~embodiment~~example according to the first ~~aspect~~example, the content of alpha-alumina is 50-100 wt**%** such as 65-95 wt%, the content of theta-alumina is 0-50 wt% such as 35-45 wt%, and the content of gamma-alumina is 0-10 wt%, such as 5 wt% or less e.g. 1 wt%, as determined by XRD, and the content of the one or more metals is 0.25-20 wt%, such as 0.25-15 wt%, 0.25-10 wt%, or 0.25-5 wt%.

The XRD (X-Ray Diffraction) is conducted according to a standard XRD analysis, in which powder X-ray diffraction patterns are collected on an XPertPro instrument configured in Bragg-Brentano mode using CuKalpha radiation, and Rietveld analysis using the TOPAS software is used to quantify the phase composition.

Without being bound by any theory, it is believed that the formation of the alpha-alumina and optionally also theta-alumina as the main alumina phases of the porous material, contrary to e.g. a predominantly gamma-alumina phase in conventional materials or catalysts, results in that the surface reactivity of the porous material towards P-species is drastically reduced. Thereby the reactivity towards P-species is also reduced so that P is not only captured on the surface of the porous material. At the same time, the porous material, showing increased pore size, allows for better penetration of the feed, in particular renewable feed, and thereby penetration of P-species. Moreover, it has also been found that the use of one or more metals having hydrotreating activity show significantly less coking on the porous material, which again, without being bound by any theory, may be attributed to the metal, e.g. Mo, blocking the remaining acidic sites or to some small hydrogenation activity of the porous material when the metal is present.

In an ~~embodiment~~example according to the first ~~aspect~~example, the porous material further comprises a compound selected from Al-borates such as Al_5BO_9, calcium aluminates, silicon aluminates, and combinations thereof. These compounds may be present in crystalline form.

In a particular ~~embodiment~~example, the sum of theta, alpha and gamma alumina and any optional of the above compounds present in crystalline form such as calcium aluminates, as determined by XRD, adds to 100 wt%.

In another particular ~~embodiment~~example, the porous material is absent of said compounds. Hence, the sum of theta, alpha and gamma alumina, as determined by XRD, adds to 100 wt%.

During preparation of the porous material, a starting (precursor) material comprising alumina and particularly having a substantial amount of gamma-alumina, such as 50 wt% or more as measured by XRD, is calcined in air at temperatures of 1050°C or higher, such as 1100°C or 1200°C or 1300°C or 1400°C, for 1-10 hours, for instance 4, 6, or 8 hours; an example being 1100°C for 2 hours, thereby transforming gamma-alumina into alpha-alumina and theta alumina. Other alumina precursors such as boehmite may also be used in the preparation, for instance as a binder.

The addition of an additive such as boric acid (H_3BO_3), a calcium containing compound, e.g. calcium nitrate ($Ca(NO_3)_2$), or silica (SiO_2) to the material during its preparation, i.e. to the starting material, allows for a better control of sintering and/or transformation to especially the alumina phase during the calcination, thereby rendering a more smooth and robust transition. Better control of the surface area and the pore size is thereby also achieved. Hence, the additive acts as a stabilizing agent during the preparation of the porous material.

When such additives are used, these are then present in the porous material as e.g. SiO_2 and/or in the alumina as e.g. Al-borate, Ca-aluminates or Si-aluminates.

In another ~~embodiment~~example, the starting material comprising alumina, for instance an alumina carrier, is a material which has been pre-calcined at temperatures of 450-850°C, preferably 450-750°C.

The guard material has some (albeit low) hydrotreating activity to avoid coking and high exothermicity when contacting the feed with the main downstream catalyst bed for hydrotreating. The most reactive molecules in the feed are converted, thereby reducing

the risk of excessive temperature rise which can lead to gumming. Hence, by the ~~invention~~disclosure a trade-off is realized: no metals will cause coking in the material, too much metal activity will cause coking and gumming due to too high exotherms. The low metal content, for instance 15 wt% Mo, 10 wt% Mo, 5 wt% Mo, or lower such as 3 wt% Mo, 1 wt% Mo, or 0.5 wt% Mo, suitably in the corresponding ranges as recited below, seems to be just right to balance out these two deactivation effects. Furthermore, some preheating prior to the feed reaching the bulk catalyst is also achieved.

In an ~~embodiment~~example according to the first ~~aspect~~example, the one or more metals comprise Mo and its content is 0.5-15 wt%, such as 0.5-10 wt%, or 0.5-5 wt%, or 0.5-3 wt%, for instance 0.5-1.5 wt% or 0.5-1 wt% such as 0.7 or 0.9 wt%, or 1-2 wt%, and optionally further comprises 0.1-5 wt%, such as 0.1-3 wt%, 0.1-1 wt%, 0.1-0.5 wt%, or 0.1-0.2 wt% of at least one of Ni, Co, and W. In another ~~embodiment~~example according to the first ~~aspect~~example, the one or more metals comprise Mo and its content is 0.5-15 wt%, such as 0.5-10 wt%, or 0.5-5 wt%, or 0.5-3 wt%, for instance 0.5-1.5 wt% such as 0.7 or 0.9 wt%, or 1-2 wt%, and optionally further comprises 0.05-0.5 wt% of Ni; optionally also the porous material does not comprise one or more metals selected from Co, W i.e. the porous material is free of Co and/or W.

In a particular ~~embodiment~~example, the at least one or more metals is Mo. In another particular ~~embodiment~~example, the one or more metals are Mo and Ni. Hence, the porous material does not comprise one or more metals selected from Co, W. For instance, the porous material may comprise 0.5-1.5 wt% Mo, such as 1 wt% Mo, and 0.1-0.2 wt% Ni. Due to the low surface area of the pore material, the Mo load (Mo content) is lowered, yet by adding e.g. Ni as promoter, it is possible to compensate for the low metal content. Furthermore, despite the low surface area of the porous material of the ~~invention~~disclosure, a small amount of molybdenum e.g. 0.5-3 wt% Mo, such as about 1 wt% results in a significantly lower coke formation. The use of molybdenum is in particular advantageous when operating with 100% renewable feedstock, as the P-capture significantly increases with respect to when the molybdenum is not present in the porous material. In addition, the presence of a small amount of nickel e.g. 0.05-0.5 wt% Ni, such as about 0.1 wt% Ni, further reduces coke formation.

The present ~~invention~~disclosure does not require the use of any metals to provide for P-capture, yet the addition of Mo turns out to reduce coking significantly and enables also the desired effect of achieving an activity gradient in the unit comprising the porous material anyway. Furthermore, while addition of Co or Ni as a promoter may be desirable since it increases activity dramatically, this may be really detrimental for the downstream hydrotreatment section comprising at least one hydrotreatment catalyst. More specifically, it may be really detrimental for hydrotreatment/hydrodeoxygenation (HDO) selectivity (yield loss) when processing renewable feedstocks. While it is desirable that oxygen removal from the renewable feedstock in the HDO proceeds mainly by removing H_2O, having particularly nickel in amounts higher than about 0.5 wt% results in undesired decarboxylation, thus reducing HDO selectivity.

The material catalytically active in hydrotreating/HDO, typically comprises an active metal (sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum, but possibly also either elemental noble metals such as platinum and/or palladium) and a refractory support (such as alumina, silica or titania, or combinations thereof).

Hydrotreating conditions involve a temperature in the interval 250-400°C, a pressure in the interval 30-150 bar, and a liquid hourly space velocity (LHSV) in the interval 0.1-2, optionally together with intermediate cooling by quenching with cold hydrogen, feed or product.

In an ~~embodiment~~example according to the first ~~aspect~~example, the BET-surface area is 1-70 m^2/g, such as 1-60 m^2/g, or 1-30 m^2/g, such as 10-30 m^2/g e.g. 15-25 m^2/g, or 1-28 m^2/g, 5-28 m^2/g, 10-28 m^2/g, 15-28 m^2/g, 20-28 m^2/g, 20-25 m^2/g, 5-20 m^2/g, or combinations thereof. Particular ~~embodiment~~examples are 3-15 m^2/g e.g. 9-10 m^2/g; or 25-30 m^2/g, 40-45 m^2/g, or 50-55 m^2/g.

In an ~~embodiment~~example according to the first ~~aspect~~example, the at least one metal is in the form of oxides or sulfides.

In an ~~embodiment~~example according to the first ~~aspect~~example, the porous material is an extruded or tabletized pellet having a shape selected from trilobal, tetralobal, pentalobal, cylindrical, spherical, hollow such as hollow rings or hollow cylinders, and combinations thereof.

Pellets having tetralobal shape, as for instance shown in Fig. 4, are particularly advantageous, due to improved outer surface area to volume ratio.

In a second ~~aspect~~example, the ~~invention~~disclosure encompasses also a process for removing one or more impurities from a feedstock, said process comprising the step of contacting said feedstock with a guard bed comprising a porous material according to any one of the preceding ~~embodiment~~examples, thereby providing a purified feedstock.

In an ~~embodiment~~example according to the second ~~aspect~~example of the ~~invention~~disclosure, the one or more impurities are selected from a vanadium-containing impurity, silicon-containing impurity, a halide-containing impurity, an iron-containing impurity, a phosphorous- containing impurity, and combinations thereof. Preferably, the one or more impurities is a phosphorous (P)-containing impurity.

In an ~~embodiment~~example according to the second ~~aspect~~example of the ~~invention~~disclosure, the process is carried out at high temperature such as 100-400°C, for instance 250-350°C, optionally in the presence of a reducing agent such as hydrogen.

In an ~~embodiment~~example according to the second ~~aspect~~example of the ~~invention~~disclosure the feedstock is:
i) a renewable source obtained from a raw material of renewable origin, such as originating from plants, algae, animals, fish, vegetable oil refining, domestic waste, waste rich in plastic, industrial organic waste like tall oil or black liquor, or a feedstock derived from one or more oxygenates taken from the group consisting of triglycerides, fatty acids, resin acids, ketones, aldehydes or alcohols where said oxygenates originate from one or more of a biological source, a gasification process, a pyrolysis process, Fischer-Tropsch synthesis, or methanol based synthesis. The oxygenates may also originate from a further synthesis process. Some of these feedstocks may contain aromatics; especially products from pyrolysis processes or waste products from e.g. frying oil. Any combinations of the above feedstocks are also envisaged.

The feedstock can also be:
ii) a feedstock originating from a fossil fuel, such as diesel, kerosene, naphtha, vacuum gas oil (VGO), spent lube oil, or combinations thereof;
or

iii) a feedstock originating from combining a renewable source according to i) and a feedstock originating from a fossil fuel according to ii)

In the context of the present ~~invention~~disclosure, the terms “renewable source” and “renewable feed” are used interchangeably.

In a particular ~~embodiment~~example, the portion of the feedstock originating from a renewable source is 5-60 wt%, such as 10 or 50 wt%. In another particular ~~embodiment~~example, the portion of the feedstock originating from a renewable source is higher than 60 wt%, for instance 70-90 wt%.

In an ~~embodiment~~example according to the second ~~aspect~~example of the ~~invention~~disclosure, the one or more impurities is a phosphorous (P)-containing impurity and said feedstock contains 0.5-1000 ppm P. The content of P may vary significantly depending on feedstock. For instance, 50-60 ppm P in oils derived from oxygenates originated from a pyrolysis process e.g. pyrolysis oil, or 100-300 ppm e.g. 200 ppm for a feedstock originating from animals, particularly animal fat.

In an ~~embodiment~~example according to the second ~~aspect~~example of the ~~invention~~disclosure, the purified feedstock is subsequently processed in a hydrotreatment stage in the presence of a hydrotreatment catalyst. In a particular ~~embodiment~~example, the hydrotreatment stage is directly downstream with optional heating/cooling in between. In another particular ~~embodiment~~example, the hydrotreatment catalyst preferably comprises at least one metal selected from Co, Mo, Ni, W and combinations thereof.

In a third ~~aspect~~example, the ~~invention~~disclosure encompasses a guard bed for a hydrotreatment system, said guard bed comprising a porous material according to the first ~~aspect~~example of the ~~invention~~disclosure.

In a fourth ~~aspect~~example, the ~~invention~~disclosure encompasses a hydrotreatment system for hydrotreating a feedstock, said hydrotreatment system comprising:
a guard bed comprising a porous material according to the first ~~aspect~~example of the ~~invention~~disclosure; and

a hydrotreatment section comprising at least one hydrotreatment catalyst, arranged downstream of said guard bed.

In a fifth ~~aspect~~example, the ~~invention~~disclosure encompasses also the use of a porous material according to the first ~~aspect~~example of the ~~invention~~disclosure as a phosphorus guard in a hydrotreatment process.

In a sixth ~~aspect~~example, the porous material is metal-free, e.g. the porous material does not comprise one or more metals selected from Co, Mo, Ni, W, and combinations thereof. The present ~~invention~~disclosure does not require the use of any metals to provide for P-capture. Accordingly, there is also provided a porous material comprising alumina,
- said alumina comprising alpha-alumina,
- said porous material not comprising one or more metals selected from Co, Mo, Ni, W, and combinations thereof,
- said porous material having a BET-surface area of 1-110 m^2/g,
wherein
- the porous material has a total pore volume of 0.50-0.80 ml/g, such as 0.50-0.75 ml/g, or 0.55-0.70 ml/g, or 0.60-0.70 ml/g, as measured by mercury intrusion porosimetry, and
- the porous material has a pore size distribution (PSD) with at least 30 vol% of the total pore volume, such as at least 40 vol%, at least 50 vol%, or at least 60 vol% being in pores with a radius ≥ 400 Å suitably in pores with a radius ≥ 500 Å, such as pores with a radius up to 5000 Å.

Any of the ~~embodiment~~examples according to the first ~~aspect~~example of the ~~invention~~disclosure may be used together with any of the ~~embodiment~~examples according to the second, third, fourth, fifth and sixth ~~aspect~~example of the ~~invention~~disclosure, or vice versa. It would also be understood, that ~~embodiment~~examples according to the first to fifth ~~aspect~~examples which are related to the use of one or more metals selected from Co, Mo, Ni, W and combinations thereof, are not used together with the sixth ~~aspect~~example of the ~~invention~~disclosure.