(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 227 387 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
16.08.2023 Bulletin 2023/33

(21) Application number: **22156772.0**

(22) Date of filing: **15.02.2022**

(51) International Patent Classification (IPC):
C10L 3/10 $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
C10L 3/108; C10L 2230/14; C10L 2270/10

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(71) Applicants:
- **TotalEnergies One Tech**
  92400 Courbevoie (FR)
- **CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE (CNRS)**
  75016 Paris (FR)

(72) Inventors:
- **Omran, Ahmed**
  14050 Caen Cedex 4 (FR)
- **Valtchev, Valentin**
  14050 Caen Cedex 4 (FR)
- **Nesterenko, Nikolai**
  1402 Nivelles (Thines) (BE)

(74) Representative: **Banse & Steglich**
Patentanwälte PartmbB
Patentanwaltskanzlei
Herzog-Heinrich-Straße 23
80336 München (DE)

(54) PROMOTION OF METHANE HYDRATE FORMATION

(57) Subject of the invention is a use of a solid Brønsted acid selected from aluminosilicates for forming methane hydrate.

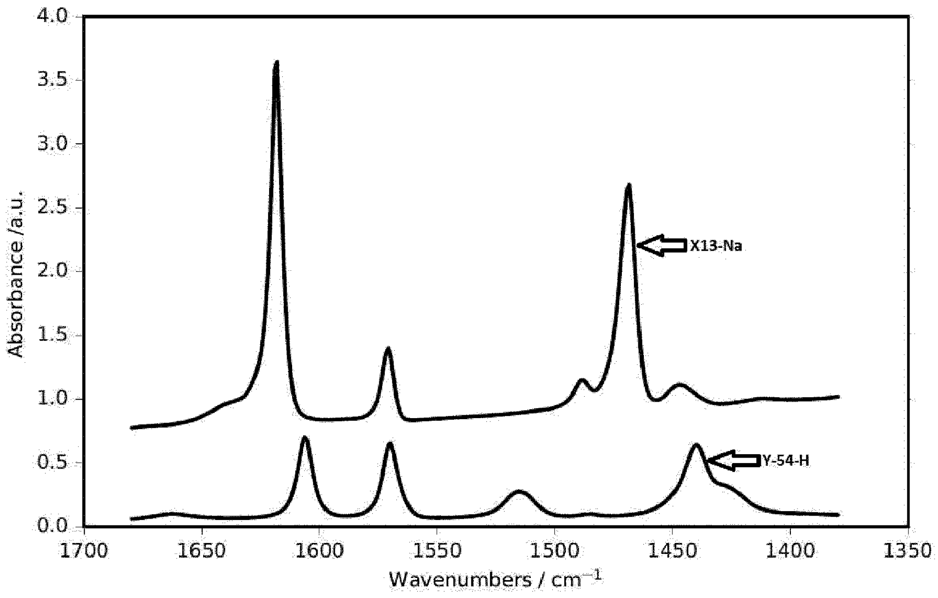

Fig. 1

Processed by Luminess, 75001 PARIS (FR)

Description

Field of the invention

[0001] The invention relates to uses of specific promoters for forming methane hydrates, to related methods and methane hydrates and to methane hydrate forming compositions.

Background of the invention

[0002] In the gas processing industry, natural gas has traditionally been stored and transported as compressed natural gas (CNG) or liquified natural gas (LNG). In both cases, the storage and transportation of the products require harsh conditions, very expensive means, and particular safety measures. For the production of LNG, low temperatures down to -161 °C are further required to liquify the natural gas and a specific regasification terminal to supply the natural gas ex LNG to the grid. Moreover, long-term storage of natural gas as LNG is regularly cumbersome due to significant losses of methane as boil-off gases. In many cases, LNG/CNG solutions would be too expensive for valorization of natural gas from inconvenient sources such as flare gas, flue gas, biogas, and shale gas.

[0003] Alternative means for natural gas storage and fractionation have thus been desired. In this context, methane hydrates (also termed methane clathrates) have been considered as a way of storing natural gas. In a methane hydrate, methane molecules are encapsulated inside cages regularly made of water molecules. The water molecules are linked by hydrogen bonds, while the hosted methane molecules are bonded via van-der-Waals forces. The cages can have different shapes, sizes and capacities, and they extend three-dimensionally into various crystal lattices. Methane hydrates are therefore at least partially crystalline.

[0004] Such crystalline methane hydrates are formed in two steps: in a first step a nucleation occurs, and in a second step the hydrate grows around the formed nucleus. Once the stable hydrates of methane are formed, they can be stored at nearly room temperate and pressure close to the atmospheric. However, the first nucleation step is regularly the critical step of the methane hydrate formation because water molecules together with methane molecules need to create a cluster of critical size. From a thermodynamic viewpoint, high pressures and/or low temperatures are regularly needed for the nucleation. Moreover, the kinetics of the nucleation step is regularly low. As a result, an economical production of methane hydrates is regularly difficult to achieve on an industrial scale due to a lack of kinetic control.

[0005] In order to address the difficulties associated with the formation of methane hydrates, thermodynamic and kinetic promoters have been investigated. Thermodynamic promoters relax the conditions for the formation of methane hydrates to lower pressures and/or higher temperatures. Such promoters can, for examples, be hydrate formers themselves, i.e., they together with water molecules build the cage surrounding a methane molecule. For example, tetrahydrofuran or tetra-n-butyl ammonium bromide can act as such a hydrate former (Zang et al., Sci China Ser B-Chem, Sep. 2008, vol. 51, no. 9, 893-900; Zhao et al., Fuel 220 (2018) 185-191; Javidani et al., Journal of Molecular Liquids 316 (2020) 113872). However, the use of hydrate formers like THF often leads to reduced storage capacities of the hydrates formed therewith.

[0006] With regard to kinetic promoters, the influence of zeolites on the formation of methane hydrates has been studied (Zang et al., Chin. J. Chem. Eng., 17(5) 854-859 (2009); Kim et al. Int. J. Energy Res. 2015; 39:26-32). The studies report only alkaline exchange zeolite, with Si/Al (atomic silicon to aluminum ratio) close to 1 and a ratio of alkali metal to Al of about 1. The studies also show that 13X zeolite is a better kinetic hydrate promoter (KHP) than both 5A and 3A zeolites. Further, the co-presence of sodium dodecyl sulfate is regularly required to achieve a successful formation of methane hydrates. Sodium dodecyl sulfate is a surfactant which can easily result in foaming which regularly impairs a long-term storage and a separation of methane from other gases. Moreover, comparably high pressures and/or low temperatures are needed for a formation of methane hydrate in the presence of the studied zeolites.

[0007] Zeolites of the Na,Cs-RHO-type have also been found to influence the formation of methane hydrates (Andres-Garcia et al., Chemical Engineering Journal 360 (2019) 569-576). This zeolite was used as synthesized without ion-exchange and was in alkaline form. However, the study does not investigate the kinetics of the hydrate formation which furthermore requires an extra pre-humidifying step before the actual conversion of methane into a hydrate, thereby making the overall process less efficient. Additionally, a cooling step from 273 K down to 243 K is required, leading to further energy consumption which makes the process less economical.

[0008] Two small pore molecular sieves which have been tested as possible promoters for methane hydrate formation are the aluminophosphate SAPO-34 and the aluminosilicate SSZ-13 (S. Denning et al., ACS Appl. Energy Mater. 2021, 4, 13420-13424). The paper is however silent about gas uptake ratios, and focuses on an adsorption of methane on the tested promoters. Moreover, a very high promotor to water ratio was tested, namely 0.2-1.2 g water/g promoter. This corresponds to 20% to 120 wt.% of employed promoter, which is a far too high amount for practical applications as it is not economical.

[0009] Overall, there remains a general desire for an improved promotion of methane hydrate formation.

Problem underlying the invention

[0010] It is an object of the present invention to provide a means of promoting methane hydrate formation which at least partially overcomes the drawbacks encountered in the art.

[0011] It is in particular an object of the present invention to provide a means of promoting methane hydrate formation which accelerates the methane hydrate formation.

[0012] It is furthermore an object of the present invention to provide a means of promoting methane hydrate formation which allows a methane hydrate formation at lower pressures and/or higher temperatures.

[0013] It is moreover an object of the present invention to provide a means of promoting methane hydrate formation which leads to a high conversion of methane into methane hydrate, allows for an improved separation of methane from other gases, requires less energy and/or requires less operational and capital expenditures.

[0014] It is also an object of the present invention to provide a method of forming a methane hydrate which at least partially overcomes the drawbacks encountered in the art.

[0015] It is also an object of the present invention to provide a methane hydrate which at least partially overcomes the drawbacks encountered in the art.

[0016] It is also an object of the present invention to provide a methane hydrate forming composition which at least partially overcomes the drawbacks encountered in the art.

Disclosure of the invention

[0017] Surprisingly, it was found that the problem underlying the invention is overcome by uses (as means), methods, methane hydrates and methane hydrate forming compositions according to the claims. Further embodiments of the invention are outlined throughout the description.

[0018] Subject of the invention is a use of a solid Brønsted acid selected from aluminosilicates for forming methane hydrate. In other words, at least methane (CH_4) and water (H_2O) are converted into methane hydrate in the presence of the solid Brønsted acid selected from aluminosilicates. The methane hydrate thus comprises CH_4 molecules hosted in cages comprising H_2O molecules.

[0019] Any use according to the present invention can also be seen as a corresponding method of using. According to the invention, "solid" excludes that the Brønsted acid or any other solid material is dissolved in a solvent. According to the invention, "solid" refers to the aggregation state of the Brønsted acid or any other solid material, in particular under normal conditions of 298.15 K and 101.3 kPa.

[0020] In the inventive use, the formation of methane hydrate in the presence of the solid Brønsted acid selected from aluminosilicate does not require, but allows the presence of other materials, in particular other solid materials. For example, additional solids like solid Brønsted acids different from aluminosilicates, solid Lewis acids or non-acidic solids may also be present when methane hydrate is formed in the inventive use.

[0021] As used herein, an aluminosilicate comprises, and preferably consists of, aluminium atoms, silicon atoms, oxygen atoms, and counter cations. Counter cations are in particular selected from alkali metal cations, alkaline earth metal cations and protons. The aluminosilicate is in particular not an aluminophosphate, the aluminosilicate does more specifically not comprise phosphor (P). The aluminosilicate used according to the present invention is a solid Brønsted acid and thus has Brønsted acidic sites, i.e., sites which function as proton donors and which are at least partially and preferably completely protonated.

[0022] According to the invention, water including crystal water does not form a Brønsted acid and has no Brønsted acidic site. According to the invention, the solid Brønsted acid preferably comprises bridging hydroxyl groups as Brønsted acidic sites.

[0023] The presence of Brønsted acidic sites can improve the kinetics of the methane hydrate formation, such that the methane hydrate is formed with shorter induction times. In other words, the presence of Brønsted acidic sites can accelerate the methane hydrate formation. Additionally, the presence of Brønsted acidic sites can lead to a high conversion of methane into methane hydrate, can allow for an improved separation of methane from other gases, may require less energy and/or may require less operational and capital expenditures.

[0024] The Brønsted acidity of the aluminosilicate used according to the present invention can be expressed in terms of the concentration of acidic cites, such that the solid Brønsted acid has a concentration of Brønsted acidic sites of $> 0\ \mu mol/g$, for example of $> 1\ \mu mol/g$, as for example determined by pyridine adsorption (Py-adsorption), in particular IR-quantified Py-adsorption.

[0025] According to the invention, the solid Brønsted acid is capable of releasing protons to its environment, for example to surrounding water, thereby regularly lowering the pH value of the environment, for example the pH of surrounding water.

[0026] It is preferred that in the inventive use, the solid Brønsted acid has a concentration of Brønsted acidic sites of $\geq 10\ \mu mol/g$, more preferred of $\geq 50\ \mu mol/g$, still more preferred of $\geq 100\ \mu mol/g$, even more preferred of $\geq 150\ \mu mol/g$ and particularly preferred of $\geq 250\ \mu mol/g$, in particular as determined by way of pyridine adsorption (as further detailed herein). Determination of the Brønsted acidic sites by pyridine adsorption is in particular preferred for cases in which the solid Brønsted acid is not a zeolite. With the mentioned continuously higher concentrations of Brønsted acidic sites, the kinetics of the methane hydrate formation can be continuously improved, the methane hydrate can be formed at continuously lower pressures and/or the methane hydrate can be formed at continuously higher temperatures. Further with such continuously higher concentrations of Brønsted acidic sites, continuously higher conversions of methane into methane hydrate may be achieved.

[0027] It is preferred that in the inventive use, the solid Brønsted acid has a concentration of Brønsted acidic sites of ≤ 9000 μmol/g, more preferred of ≤ 3500 μmol/g, still more preferred of ≤ 3000 μmol/g, even more preferred of ≤ 2000 μmol/g and particularly preferred of ≤ 1000 μmol/g, in particular as determined by way of pyridine adsorption (as further detailed herein). A solid Brønsted acid may be formed by converting a non-Brønsted acidic solid into a solid Brønsted acid. When the targeted concentrations of Brønsted acidic cites become higher, severer conditions for the conversion may be required. Such severer conditions may require more energy. With the mentioned upper limits of the concentration of Brønsted acidic sites, such an undesired energy demand becomes continuously lower.

[0028] It is preferred that in the inventive use, the solid Brønsted acid has a concentration of Brønsted acidic sites of ≥ 10 μmol/g to ≤ 9000 μmol/g, more preferred of ≥ 50 μmol/g to ≤ 3500 μmol/g, still more preferred ≥ 100 μmol/g to ≤ 3000 μmol/g, even more preferred of ≥ 150 μmol/g to ≤ 2000 μmol/g and particularly preferred of ≥ 250 μmol/g to ≤ 1000 μmol/g, in particular as determined by way of pyridine adsorption (as further detailed herein). With such ranges, the kinetics of the methane hydrate formation can be continuously improved, the methane hydrate can be formed at continuously lower pressures and/or the methane hydrate can be formed at continuously higher temperatures. Further with such ranges, continuously higher conversions of methane into methane hydrate can be achieved. Simultaneously, with such ranges an undesired energy demand for the formation of acidic sites may become continuously lower.

[0029] It is preferred that in the inventive use, the solid Brønsted acid is a zeolite. Zeolites are well-known Brønsted solid acids comprising silicon atoms, aluminium atoms and oxygen atoms as well as alkali metal atoms and/or alkaline earth metal atoms. The concentration of Brønsted acidic sites in such zeolites can be assumed to be equal to the concentration the aluminium atoms in the structure minus the concentration of the alkali/alkaline earth metal(s) divided by their degree of oxidation. As such, the acidity of the solid Brønsted acid used according to the invention requires no pyridine measurement but can for example be inferred from the aluminium concentration, especially from the ratio of silicon atoms to aluminium atoms (Si/Al ratio). Such acidic zeolites are also referred to as zeolites in H-form, i.e., in at least partially protonated form in which the alkali metal atoms and/or alkaline earth metal atoms are at least partially substituted by protons (or ammonium cations; NH_4^+). For example, for a zeolite with Si/Al > 2 in H-form (H^+-form and/or NH_4^+-form, in particular H^+-form), the concentration of the Al sites can be up to 9000 μmol/g, (i.e., Al concentration of ≤ 9000 μmol/g), corresponding to a concentration of Brønsted acidic sites of ≤ 9000 μmol/g.

[0030] It is preferred that in the inventive use, the solid Brønsted acid is a zeolite in which at least 10% of all Al-sites, more preferred at least 20% of all Al-sites, and still more preferred at least 30% of all Al-sites are in H-form. More specifically, another possibility to express the acidity of a zeolite as a solid Brønsted acid used according to the invention is a molar ratio of alkali metal and/or alkaline earth metal comprised by the zeolite divided by the degree of their respective oxidations (divided by their oxidation state) to the number of Al atoms in the framework of the zeolite. It is preferred that in the inventive use, such a ratio is ≤ 0.9, more preferred ≤ 0.8 and still more preferred ≤ 0.7. This ratio can in particular be determined by elemental analysis. Such a ratio means that at least 10%, 20% or 30%, respectively, of the available Brønsted acid sites are protonated, i.e., are present in H-form (H^+-form and/or NH_4^+-form, in particular H^+-form). Expressed differently, the concentration of exchange metal (alkali and/or alkaline earth) divided by its degree of oxidation is at least 10%, 20% or 30%, respectively, less than the amount of Al in the zeolite framework. It has been shown that the use of zeolite in such H-form allows for a good control of the kinetics to synthesise methane hydrates.

[0031] The solid Brønsted acid may additionally comprise Lewis acidic sites, preferably in a concentration of ≥ 20 μmol/g, more preferably of ≥ 30 μmol/g. As the skilled person is well aware, a Lewis acid is capable of accepting an electron pair.

[0032] In the inventive use, the solid Brønsted acid is selected from aluminosilicates, in other words the solid Brønsted acid is made of an aluminosilicate. As used herein, "made of" does not mean that the solid Brønsted acid consists of an aluminosilicate, especially zeolite. Rather, the solid Brønsted acid comprises an aluminosilicate, especially zeolite, typically as a major component. The solid Brønsted acid may therefore be composed of ≥ 50 wt.%, preferably of ≥ 60 wt.%, more preferably of ≥ 70 wt.%, even more preferably of ≥ 80 wt.% and still more preferably of ≥ 90 wt.% of aluminosilicate, especially zeolite; the weight percentages are based on the total dry weight of the solid Brønsted acid. In a particular case, the solid Brønsted acid consists of an aluminosilicate, especially zeolite.

[0033] It is preferred that in the inventive use, the solid Brønsted acid is made of a zeolite (molecular sieve). When the solid Brønsted acid is made of zeolite, the solid Brønsted acid may be provided at low handling costs, thereby improving the economics of the inventive use. When the solid Brønsted acid is made of a zeolite, the kinetics of the methane hydrate formation and/or the conversion ratio of methane into hydrate may be further improved. When the solid Brønsted acid is made of a zeolite, the methane hydrate formation may be possible at fast kinetics and higher gas-to-hydrate conversion. When the solid Brønsted acid is made of a zeolite, a contamination of an aqueous solution used for methane hydrate formation can be avoided, and a recycling of the solid Brønsted acid may be simplified. Additionally, zeolites may be re-used, which can improve the economic efficiency of the inventive use.

[0034] In an embodiment, the zeolite could be used in shaped form, i.e., as a shaped zeolite. A shaped zeolite can facilitate its handling. Preferably, the zeolite is used in a shaped form selected from extrudates, bids, or pellets. The shaped form can also contain alumina, silica, silica-alumina, zirconia, clay(s) or a mixture thereof. A shaped zeolite can allow for an easy separation, e.g., by filtration.

[0035] It is preferred that in the inventive use, the solid Brønsted acid is made of a zeolite having a ratio of silicon to aluminium atoms (Si/Al) of > 2. Such a zeolite is typically moderately hydrophobic. When the solid Brønsted acid is made of a zeolite having an Si/Al-ratio of > 2, the kinetics of the methane hydrate formation and/or the conversion ratio of methane into hydrate may be further improved. Further, zeolites with a ratio Si/Al < 1.5 are typically not stable in H-form, too hydrophilic, and often become amorphous in the presence of water which is regularly detrimental to a formation of methane hydrates. On the other hand, a zeolite having a high Si/Al ratio may be obtained by dealumination of a zeolite having a lower Si/Al-ratio. An excessive dealumination may however impair the structural integrity of the zeolite and hence its functioning in the inventive use. It is therefore preferred that the zeolite has a ratio of Si/Al of ≤ 100, more preferred of ≤ 75 and still more preferred of ≤ 50. In order to achieve a balance between high conversion ratio and stable H-form on the one hand and structural integrity of the zeolite on the other hand, it is particularly preferred that the zeolite has ratio of Si/Al of 2 < Si/Al ≤ 100, more preferred of 25 ≤ Si/Al ≤ 75 and still more preferred of 5 ≤ Si/Al ≤ 50.

[0036] It is preferred that in the inventive use, the zeolite is selected from FAU-type zeolite, (for example zeolite Y), MFI-type zeolite (for example ZSM-5, boralite C, TS-1), MEL-type zeolite (for example ZSM-11, boralite D, TS-2, SSZ-46), ZSM-8, MOR, FER-type zeolite (for example Ferrierite, FU-9, ZSM-35), MTT-type zeolite (for example ZSM-23), TON-type zeolite (for example ZSM-22, Theta-1, NU-10), EUO-type zeolite (for example ZSM-50, EU-1), MFS-type zeolite (for example ZSM-57), BEA-type zeolite (for example BETA), ZSM-48, CHA-type zeolite (for example SSZ-13), AEI-type zeolite (for example SSZ-39), ERI-type zeolite, MTW-type (ZSM-12), MWW-type (MCM-22) and mixtures thereof. The zeolite types are indicated by the codes attributed by the International Zeolite Association.

[0037] It is in particular preferred that in the inventive use, the solid Brønsted acid is a FAU-type zeolite, an MFI-type zeolite, a CHA-type zeolite or an MOR-type zeolite, preferably a FAU-type zeolite.

[0038] It is preferred that in the inventive use, the solid Brønsted acid is made of a FAU-type zeolite (which is at least partially in H-form). A FAU-type zeolite has a faujasite framework. The faujasite framework has the basic formula $(Na_2,Ca,Mg)_{3\text{-}5}[Al_7Si_{17}O_{48}]\cdot 32(H_2O)$. The amounts of sodium (Na), calcium (Ca) and magnesium (Mg) may vary, and aluminium (Al) atoms may be partly removed by dealumination. In this case, the solid Brønsted acid is generated in FAU-type zeolite by exchanging Na, Ca and Mg to protons. In this case, the kinetics of the methane hydrate formation and/or the conversion ratio of methane into hydrate may be further improved.

[0039] It is preferred that in the inventive use, the solid Brønsted acid is made of a Y-type zeolite (also termed zeolite Y). The Y-type zeolite is a specific FAU-type zeolite which has large, substantially spherical, internal cavities (also termed super cages) linked tetrahedrally through pore openings and defined by rings of twelve oxygen atoms. The sodium form (also termed NaY) has a cubic unit cell containing 192 $(Si, Al)O_4$ tetrahedrons. The zeolite Y in acidic form is available commercially, for example, under the trade names of a US-Y-40, a CBV714, a CBV400, a CBV600, a CBV712, a CBV720, a CBV740, a CBV760, a CBV780, a CBV901 zeolite or a Y-54 zeolite. Without wishing to be bound by theory, it is assumed that a Brønsted acidic Y-type zeolite allows for a particularly good exchange of cations in a methane hydrate forming composition by protons, which are assumed to have a positive impact on the kinetics and/or on the thermodynamics of a methane hydrate formation. Thus, when the solid Brønsted acid is made of a Y-type zeolite, the kinetics of the methane hydrate formation and/or the conversion ratio of methane into hydrate may be further improved.

[0040] It is preferred that in the inventive use, the solid Brønsted acid is made of an aluminosilicate, preferably a zeolite, having a BET surface (S_{BET}) of ≤ 1000 m^2/g. Such a surface may improve the interaction of the Brønsted acidic sites of the solid Brønsted acid with a surrounding aqueous solution when forming methane hydrate.

[0041] It is preferred that in the inventive use, the solid Brønsted acid is made of an aluminosilicate, preferably a zeolite, having an external surface (S_{ext}) of ≥ 10 m^2/g. Such a surface may improve the interaction of the Brønsted acidic sites of the solid Brønsted acid with a surrounding aqueous solution when forming methane hydrate.

[0042] It is preferred that in the inventive use, the solid Brønsted acid is made of an aluminosilicate, preferably a zeolite, having a volume of micropores (V_{micro}) of ≤ 0.4500 cm^3/g. Such a volume of micropores may improve the interaction of the Brønsted acidic sites of the solid Brønsted acid with a surrounding aqueous solution when forming methane hydrate.

[0043] It is preferred that in the inventive use, the solid Brønsted acid is made of an aluminosilicate, preferably a zeolite, having a volume of mesopores (V_{meso}) of ≥ 0.0100 cm^3/g. Such a volume of mesopores may improve the interaction of the Brønsted acidic sites of the solid Brønsted acid with a surrounding aqueous solution when forming methane hydrate.

[0044] Accordingly, it is particularly preferred that in the inventive use, the solid Brønsted acid is made of an aluminosilicate, preferably a zeolite, having an S_{BET} of ≤ 1000 m^2/g, an S_{ext} of ≥ 10 m^2/g, a V_{micro} of ≤ 0.4500 cm^3/g, and a Vmeso of ≥ 0.0100 cm^3/g.

[0045] It is preferred that in the inventive use, the solid Brønsted acid contains ≤ 10 wt.% Na, more preferably ≤ 5 wt.% Na, as determined by EDX (as further detailed herein). When the solid Brønsted acid contains such low amounts of Na, the kinetics of the methane hydrate formation may be further improved.

[0046] It is preferred that in the inventive use, the solid Brønsted acid has a concentration of Na of ≤ 2.0000 mg/l, more preferably of ≤ 1.0000 mg/l, as determined by inductively coupled plasma measurement (as further detailed herein). When the solid Brønsted acid has such low concentrations of Na, the kinetics of the methane hydrate formation may be further improved.

[0047] It is preferred that in the inventive use, the solid Brønsted acid has a water activity a_w of ≥ 0.9400, more preferred of ≥ 0.9410, even more preferred of ≥ 0.9420 and particularly preferred of ≥ 0.9430 (determined as further detailed herein). With such a water activity, the induction time of a methane formation can be further shortened.

[0048] It is preferred that in the inventive use, the methane hydrate is formed in the presence of a hydrate former different from water. With the use of another hydrate former in addition to water, the methane hydrate formation may be possible at higher temperatures and/or lower pressures. It is particularly preferred that the hydrate former is selected from tetrahydrofuran, cyclopentane, tetra-n-butyl ammonium bromide, propylene oxide, 1,4-dioxane and cyclooctane. With such a particular hydrate former even lower pressures and/or higher temperatures may be possible during the methane hydrate formation. The most preferred hydrate former is tetrahydrofuran which may allow for still lower pressures and/or higher temperatures during the methane hydrate formation.

[0049] It is preferred that in the inventive use, the methane hydrate is formed at a pressure below 8 MPa, more preferably ≤ 6 MPa, and/or at a temperature above 280 K, more preferably ≥ 283 K. With such relaxed conditions for forming the methane hydrate, energy savings may be possible, leading to an improved economic efficiency of the inventive use.

[0050] It is preferred that in the inventive use, the methane hydrate is formed in the absence of sodium dodecyl sulfate (SDS), preferably in the absence of an anionic surfactant and more preferably in the absence of a surfactant. The absence of surfactants, in particular the absence of anionic surfactants like SDS, may avoid the occurrence of foaming during a methane hydrate formation. As foaming may worsen the kinetics, the thermodynamics and/or the economic efficiency of methane hydrate formation, such detrimental effects can be avoided when no surfactant and in particular no anionic surfactant like SDS is present in the inventive use.

[0051] It is preferred that in the inventive use, the solid Brønsted acid has a concentration of Brønsted acidic sites of ≥ 100 to ≤ 2000 μmol/g, wherein the solid Brønsted acid is a Y-type zeolite having a ratio of 2 < Si/Al < 100, and wherein the methane hydrate is formed in the presence of tetrahydrofuran. With such a use, the effects with respect to accelerated methane hydrate formation, high conversion of methane into methane hydrate, separation of methane from other gases, less energy consumption and/or less operational and capital expenditures may be particularly pronounced.

[0052] In the inventive use, a mixture comprising methane (CH_4) and water (H_2O) is converted into methane hydrate in the presence of the solid Brønsted acid. It is preferred that the composition composed of the mixture and the solid Brønsted acid contains ≥ 0.001 wt.% of the solid Brønsted acid, more preferably ≥ 0.001 wt.% to ≤ 2 wt.% of the solid Brønsted acid, based on the total weight of the composition. With such amounts of solid Brønsted acid, the effects of the solid Brønsted acid described herein can be achieved while avoiding unnecessary high amounts thereof, which can improve the economic efficiency of the methane hydrate formation.

[0053] It is preferred that in the inventive use, a methane uptake of ≥ 52 mmol CH_4/mol H_2O, more preferably of ≥ 53 mmol CH_4/mol H_2O, still more preferably of ≥54 mmol CH_4/mol H_2O and most preferably of ≥ 60 mmol CH_4/mol H_2O is realized. With such methane uptakes, the economic efficiency of the inventive use can be further improved.

[0054] It is preferred that in the inventive use, a conversion of methane into methane hydrate of ≥ 90%, more preferably of ≥ 92% and still more preferably of ≥ 94% is realized. With such conversions of methane into methane hydrate, the economic efficiency of the inventive use can be further improved.

[0055] Subject of the invention is also method of forming a methane hydrate, comprising the steps:

i) providing a solid Brønsted acid selected from aluminosilicates, and
ii) converting a mixture comprising water and methane into a methane hydrate in the presence of the solid Brønsted acid provided in step i). Logically, step ii) follows step i).

[0056] With such a method it can be possible to form methane hydrate at shorter induction times and/or with a high conversion of methane into methane hydrate. Such a method may also allow for an improved separation of methane from other gases, and may require less energy and/or may require less operational and capital expenditures for the formation of methane hydrate.

[0057] It is preferred that before step i), an aluminosilicate having no Brønsted acidic sites is converted into the solid Brønsted acid provided in step i). For example, when the solid Brønsted acid is made of a zeolite, a non-Brønsted acidic zeolite is converted into a Brønsted acidic zeolite. This can for example be achieved by ion exchange in an aqueous solution of an ammonia salt like NH_4NO_3 or NH_4Cl. In a first step, metal cations in the Brønsted non-acidic zeolite are replaced by NH_4^+-ions. In a second step, ammonia is removed by calcination, leaving a protonated site behind, namely a Brønsted acidic site. With such a conversion, a cheap solid material may be used which can then be converted into the desired solid Brønsted acid for the purposes of the present invention. Such a conversion may lead to reduced costs and a more feasible formation of the solid Brønsted acid.

[0058] The preferred embodiments of the inventive use described herein including the claims are likewise preferred for the inventive method of forming a methane hydrate in an analogous manner.

[0059] Subject of the invention is also a methane hydrate which is obtainable by an inventive use, or which is obtainable by an inventive method. Such a methane hydrate may be formed at shorter induction times and/or with a high conversion of methane into the methane hydrate. Such a methane hydrate may also allow for an improved separation of methane from other gases, and may require less energy and/or may require less operational and capital expenditures for its formation.

[0060] A methane hydrate formed according to the invention generally comprises CH_4 molecules hosted in cages comprising H_2O molecules. In addition, also hydrogen (H_2) and/or carbon dioxide (CO_2) molecules may be comprised by the formed methane hydrate, which molecules are then likewise hosted in cages comprising H_2O molecules. This general possibility of an additional presence of H_2 and/or CO_2 molecules applies to all inventive aspects and embodiments provided herein.

[0061] It can be preferred that the methane hydrate is a sII hydrate. Methane hydrates can commonly be in the form of structure I (sI), structure II (sII), structure H (sH) and semiclathrate. An sII methane hydrate can be a hydrate in which the guest molecules are not exclusively gas molecules, but incorporates into the cage further compounds, which are herein referred to as a "hydrate former" or "thermodynamic promoter". Such an sII hydrate may have thermodynamic advantages and may in particular be formed at lower pressures and/or higher temperatures. It can be particularly preferred that the methane hydrate is a sII hydrate which comprises tetrahydrofuran (THF) as a hydrate former. Such an sII hydrate comprising THF may be formed at even lower pressures and/or even higher temperatures.

[0062] The preferred embodiments of the inventive use described herein including the claims are likewise preferred for the inventive methane hydrate in an analogous manner.

[0063] Subject of the invention is also a methane hydrate forming composition comprising methane, water and a solid Brønsted acid selected from aluminosilicates. The Brønsted acid selected from aluminosilicates may optionally be combined with a binder, wherein the binder is preferably alumina, silica, silica-alumina, zirconia, clay(s) or a mixture thereof. With such a methane hydrate forming composition, it can be possible to form methane hydrate at shorter induction times, at lower pressures and/or higher temperatures, and/or with a high conversion of methane into methane hydrate. Such a methane hydrate forming composition may also allow for an improved separation of methane from other gases, and may require less energy and/or may require less operational and capital expenditures for the formation of methane hydrate.

[0064] It is preferred that the methane hydrate forming composition contains ≥ 0.001 wt.% of the solid Brønsted acid, more preferably ≥ 0.001 wt.% to ≤ 2 wt.% of the solid Brønsted acid, still more preferably ≥ 0.001 wt.% to ≤ 0.500 wt.% of the solid Brønsted acid, and in particular preferably ≥ 0.001 wt.% to ≤ 0.250 wt.% of the solid Brønsted acid, based on the total weight of the composition. With such amounts of solid Brønsted acid, the effects of the solid Brønsted acid described herein can be achieved while avoiding unnecessary high amounts thereof, which can improve the economic efficiency of the methane hydrate formation. The mentioned effects can be particularly pronounced in case the composition contains ≥ 0.001 wt.% to ≤ 0.500 wt.% of the solid Brønsted acid, wherein the solid Brønsted acid is a zeolite having a concentration of Brønsted acidic sites of > 50 μmol/g.

[0065] The preferred embodiments of the inventive use described herein including the claims are likewise preferred for the inventive methane hydrate forming composition in an analogous manner.

Applications and further advantages

[0066] The present invention aims at a methane hydrate conversion which improves the conversions known in the art, thereby reducing the amount of gas which needs to be recompressed for recycling. The present invention can further be used for storing and transporting methane in solid form which can be a safer and more controllable form of storing and transporting methane. The present invention can be used for long term storage of methane because methane hydrates can be stored at temperature near ambient at minimum pressure. Storing methane as a hydrate can be applied in modular mode, which allows an easy installation in remote areas. The present invention merely requires a simple setup in non-stirred reactor configuration so that the energy consumption can be limited. Additionally, the storage of methane can in one step be combined with a separation thereof from other gases. On an industrial scale, less operational and capital expenditures may be required, and the invention can be applied at basically any location and without a necessity to use a separate gas terminal.

Brief description of the drawings

[0067]

Fig. 1 shows an IR-spectrum obtained in acidity measurements of two zeolites.
Fig. 2 shows a summary of EDX-spectra of Y-54-H zeolite and X13-Na zeolite samples.
Fig. 3 shows a PXRD-pattern of a Y-54-H zeolite.
Fig. 4 shows a PXRD-pattern of a X13-Na zeolite.
Fig. 5 shows a methane hydrate formation and dissociation apparatus.
Fig. 6 shows an NMR-spectrum of a methane hydrate.
Fig. 7 shows a PXRD-pattern of a methane hydrate.
Fig. 8 shows a Raman-spectrum of a methane hydrate, Fig. 9 shows a first subsection of the Raman-spectrum, and Fig. 10 shows a second subsection of the Raman-spectrum.
Fig. 11 shows a comparison of induction times for different promoters.
Fig. 12 shows a comparison of methane uptakes for different promoters.
Fig. 13 shows a comparison of methane conversions for different promoters.

Materials and Methods

Concentration of acidic sites

[0068] Acidity was first measured by pyridine (Py) adsorption which is quantified via infrared (IR) measurements (IR-quantified Py-adsorption). IR spectra were recorded on a Nicolet Magna 550 Fourier-Transform (FT)-IR spectrometer with 4 cm^{-1} optical resolution, with one level of zero-filling for the Fourier transform. Prior to the measurements, the samples were pressed in self-supporting discs (diameter: 1.6 cm, 10 mg cm^{-2}) and activated in the IR cell (attached to a vacuum line) at 723°K for 4 h up to 106 Torr (14132.17 Pa). The IR cell was equipped with KBr windows, which allowed registering the spectra in the spectral region down to 400 cm^{-1}. The pressure of the adsorbed gases was measured by two Barocel gauges. One gauge was attached directly to the sample containing compartment of the cell. Another gauge allowed to measure a dose of gas in the known volume before adsorption thereof into the cell. The sample temperature during the treatment or recording of spectra was monitored by a chromel-alumel thermocouple inserted into the heater or into the coolant compartment of the cell. Adsorption of Py was performed at 423°K. The excess of probe molecules was further evacuated at 423°K. The adsorption-evacuation was repeated several times until no changes in the spectra were observed. The amount of the adsorbed Py was measured by means of the extinction coefficients ε_{1545} (at 1545 cm^{-1}; pyridine attached to Brønsted acidic sites) = 1.8 cm/μmol and ε_{1455} (at 1455 cm^{-1}; pyridine attached to Lewis acidic sites) = 1.5 cm/μmol. The pyridine adsorption allowed quantifying the Brønsted acidic sites via ε_{1545} and the Lewis acidic sites via ε_{1455}.

^{27}Al NMR to measure the amount of Al atoms in the framework

[0069] The Al in the zeolite framework was determined from combinations of data from elemental analysis and ^{27}Al MAS NMR data. The total amount of Al measured by elemental analysis was multiplied by the fraction of the signal of ^{IV} Al (50-55 ppm) in NMR spectrum relative to the total surface of the peaks. NMR measurements were done with 4 mm (outer diameter; herein also abbreviated "o.d.") zirconia rotors and with a spinning speed of 12 kHz on a Bruker Avance 400 spectrometer operating at 100.6 MHz, while a 1 M $Al(NO_3)_3$ solution was used for ^{27} Al. The quantification of the obtained spectra was done by the integration of the peak area using a Dmfit program.

Chemical Composition and Si/Al framework molar ratio

[0070] The chemical composition and Si/Al-ratio was determined using inductively coupled-atomic plasma emission spectroscopy (ICP-AES) on an OPTIMA 300 DV (Perkin-Elmer) and scanning electron microscopy-based energy dispersive X-ray (EDX) spectroscopy.

Surface area and volume of pores

[0071] In general, the surface area and the porous volume can be measured via N_2-adsorption using usual surface area measurements. In particular, surface area measurements such as a BET-measurement (measurement according Brunauer, Emmet, Teller) can be used (ASTM D3663 for the surface area; and ASTM D4365 for the porous volume). In the present case, nitrogen adsorption measurements were performed on Micromeritics® ASAP 2020 surface area analyzer. The isotherms were obtained using ASAP 2020 analysis program. The external surface (S_{ext}) and the volume of micropores (V_{micro}) were obtained from t-plot based on the Harkins-Jura equation.

X-ray diffraction measurements

[0072] Powder X-ray diffraction (PXRD) patterns were obtained with a PANalytical X'Pert Pro® diffractometer system using Cu-Kα1-radiation (λ = 1.5418 Å; 45 kV; 40 mA) in a continuous scan at 25°C. Start position in 2Theta = 5.0084° for the solid promoters and 10.0114° for the hydrate. End position in 2Theta = 49.9734° for the solid promoters and 39.7500° for the hydrate. Step size in 2Theta = 0.0170°, scan step time = 50.1650 s. The measured specimen had a length of 10 mm. For analysing the hydrate, the sample was grounded by mortar and pestle to prepare a uniform hydrate powder (using a liquid nitrogen environment to prevent hydrate dissociation).

NMR spectroscopy

[0073] Solid state ^{13}C MAS NMR spectra were obtained using a Bruker DRX400 spectrometer at a Larmor frequency of 100.6 MHz. Spectra were recorded at 250 K by placing the powdered hydrate samples in a 4 mm o.d. Zr-rotor that was loaded into a variable-temperature (VT) probe. All ^{13}C NMR spectra were recorded with magic angle spinning (MAS) between 2 and 4 kHz.

Raman Spectroscopy

[0074] Raman spectra were obtained using an immersion Raman probe (InPhotonics) lined to the spectrometer (Horiba LabRam Evol) via optical fibres. A green laser at 532 nm wavelength was used for excitation. The spectral coverage is 50-3500 cm^{-1}.

Water activity

[0075] The water activity of solutions/dispersions was measured according to Ho-Van et al., "Experimental measurement and thermodynamic modeling of cyclopentane hydrates with NaCl, KCl, CaCl2, or NaCl-KCl present"; AIChE J, 64: 2207-2218, 2018.

Materials

[0076] Methane (99.99% purity) was purchased from Linde Co., Tetrahyrofuran (THF, AR grade 99.99%) from Alfa Aesar, X13-Na (Molecular Sieve Union Carbide Type 13 X) from Fluka AG, Y-54-Na zeolite from UOP, and deionized water used for different aqueous solution was obtained from Laboratoire Catalyse & Spectrochimie (LCS), ENSICAEN. The acidic form Y-54-H was prepared by exchanging Y-54-Na 5 times with 10 wt.% NH_4NO_3 (yielding Y-54-NH_4) and calcining the obtained zeolite at 450°C for 4 hours.

Examples

Characterisation of solids (promotors)

[0077] The acidity of the Y-54-H zeolite and of the X13-Na zeolite were determined by pyridine adsorption quantified via infrared measurements as described herein. Table 1 below reports the results for the two extinction coefficients ε_{1545} (Brønsted acidic sites) and ε_{1455} (Lewis acidic sites) and the total acidities. Fig. 1 shows the corresponding IR-spectra.

Table 1

Zeolite	ε_{1545} (μmol/g)	ε_{1455} (μmol/g)	Total acidity (μmol/g)
Y-54-H	283	464	747
X13-Na	-	353	353

[0078] The BET-surface (S_{BET}), the external surface (S_{ext}), the volume of micropores (V_{micro}), the volume of mesopores (V_{meso}), and the total volume of pores (V_{total}) of the Y-54-H zeolite and of the X13-Na zeolite were determined as described herein. Table 2 below reports the respective results.

Table 2

Zeolite	S_{BET} (m^2g^{-1})	S_{ext} (m^2g^{-1})	V_{micro} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	V_{total} (cm^3g^{-1})
Y-54-H	446	65	0.147538	0.046527	0.194065
X13-Na	833	54	0.298131	0.034619	0.33275

[0079] Energy dispersive X-ray spectroscopy (EDX) measurements were also performed to characterize the Y-54-H zeolite and the X13-Na zeolite. For the Y-54-H zeolite, three different samples were measured. Table 3 below reports the results of the elemental analyses (Al = aluminium; Si = silicon; Na = sodium; rounded to two decimal places).

[0080] Fig. 2 represents a summary of the results of the EDX measurements.

Table 3

Element	Net	Mass%	Mass% (normalized)	Atom%	Absolute error in % (1 sigma)	Relative error in % (1 sigma)
Y-54-H (sample #1)						
Al	328805	5.28	26.83	27.39	0.28	5.25
Si	849005	13.64	69.24	67.90	0.61	4.44
Na	24756	0.77	3.93	4.70	0.08	9.86
	Total:	19.69	100.00	100.00		
Y-54-H (sample #2)						
Al	146766	6.94	25.55	26.11	0.36	5.15
Si	375371	19.24	70.79	69.50	0.84	4.39
Na	11976	1.00	3.67	4.40	0.09	9.30
	Total:	27.17	100.00	100.00		
Y-54-H (sample #3)						
Al	240420	9.32	25.18	25.82	0.47	5.05
Si	618582	26.90	72.66	71.58	1.17	4.35
Na	12025	0.80	2.16	2.60	0.08	9.95
	Total:	37.03	100.00	100.00		
X13-Na						
Al	311131	19.60	34.57	33.67	0.96	4.90
Si	368444	23.10	40.73	38.11	1.01	4.37
Na	174806	14.00	24.69	28.22	0.93	6.62
	Total:	56.70	100.00	100.00		

[0081] Inductively coupled plasma measurements were also performed to characterize the Y-54-H zeolite and the X13-Na zeolite. Table 4 below reports the respective results.

Table 4

	^{23}Na [HEHe]	^{27}Al [HEHe]	^{29}Si [HEHe]
Zeolite	Concentration [mg/l]	Concentration [mg/l]	Concentration [mg/l]

(continued)

	^{23}Na [HEHe]	^{27}Al [HEHe]	^{29}Si [HEHe]
X13-Na	5.535117605	6.550813348	8.165362365
Y-54-H	0.776878302	4.94501044	13.27590053

[0082] PXRD measurements were also performed to characterize the Y-54-H zeolite and the X13-Na zeolite. The obtained PXRD-pattern of the Y-54-H zeolite is shown in Fig. 3, and the obtained PXRD-pattern of the X13-Na zeolite is shown in Fig. 4.

[0083] In order to further determine the Brønsted acidity of the materials used herein, pH-measurements were performed. More specifically, as a blank sample an aqueous solution of THF (5.56 mol%) was prepared. Additionally, two other samples of THF aqueous solutions (5.56 mol% THF) of 0.5 wt.% of X13-zeolite, and 0.5 wt.% of the Y-54 zeolite in protonated form (Y-54-H) were prepared in volumetric flasks. At 25°C, a calibrated pH meter (HI 2210 pH meter, Hanna Instruments) was used to measure pH values of the above samples. Table 5 below reports the respective results.

Table 5

	Blank THF (5.56 mol% THF)	0.5 wt.% 13X-Na zeolite at 5.56 mol% THF solution	0.5 wt.% Y-54-H zeolite at 5.56 mol% THF solution
pH value at 25°C	7.5	9.19	4.52

Hydrate Formation

[0084] As a blank sample, an aqueous solution of THF (5.56 mol%) was prepared. Additionally, aqueous solutions (including 5.56 mol% THF) of the X13-zeolite, of the Y-54 zeolite in protonated form (Y-54-H), in protonated form together with sodium dodecyl sulfate (Y-54-H-SDS; concentration of SDS was 200 ppm) and in ammonia-exchanged form (Y-54-NH_4) were prepared in volumetric flasks. At 25°C, the water activity (a_w) was 0.9390 for the X13-zeolite, and 0.9435 for the Y-54-H zeolite.

[0085] The used methane hydrate formation and dissociation apparatus shown in Fig. 5 consisted of a 450 cm^3 high-pressure stainless-steel reactor (CR; Parr) which was immersed in a cooling bath. An external refrigerator (ER; Julabo, F250) circulated a glycol solution to control the temperature of the cooling bath. A pressure transmitter (PT; UNIK 5000, GE) with a range of 0-30 MPa and 0.1 % global error was used to measure the system pressure, while a K-type thermocouple (T) with ±1.0 K accuracy was used to monitor the temperature. A data logger (DAQ; Nanodac, Eurotherm) was connected to a personal computer (PC) to record the data during the experiment. All experiments were repeated three times to ensure consistency and were carried out with a fixed amount of gas and solution of 228 cm^3 in a closed system (isochoric system).

[0086] Each experiment used 228 cm^3 of solution, and the seal of the reactor was tightened. The reactor was purged three times with N_2 and then with methane to ensure air removal from the system. After the required temperature (283.2 K) and pressure (6 MPa) were achieved, their values were recorded every 10 sec with the DAQ system. The period of time between this starting point and the formation of the first hydrate crystal is referred to as the 'induction time'. The induction time can be determined by a simultaneous pressure drop and temperature increase due to the exothermic nature of the hydrate formation. As the reaction continues the pressure drops further, and the hydrate formation process is considered complete when there is no further drop for 1 h.

[0087] The moles of methane consumed in hydrate and gas-to-hydrate conversion were calculated using the pressure and temperature data recorded during the period of the experiment. Calculation details are reported for example in Najibi et al., Journal of Natural Gas Science and Engineering, 2015, 23, 315-323.

[0088] A ^{13}C MAS NMR spectrum of the methane hydrate obtained at 283 K and 6 MPa using an Y-54-H promoter is shown in Fig. 6. Methane molecules occupied only small cages and appeared at about -4.3 ppm. THF molecules occupied large cages and were represented by two resonances (-C-C- at 26.0 ppm, -C-O-C- at 68.3 ppm). The increase of integration ratio (CH_4:THF) from 0.90:2.00 in the case of using X13-Na to 1.25:2.00 in the case of Y-54-H indicates that methane cage occupancy and hence storage capacity is improved by the use of a solid Brønsted acid.

[0089] The PXRD-pattern of the methane hydrate obtained with the Y-54-H zeolite is shown in Fig. 7. The formed methane hydrate was characterised using powder X-ray diffraction as detailed herein (see methods section). The experimental conditions of pressure and temperature were chosen to stay in the stability boundary of sII hydrates and to avoid a formation of thermodynamically less stable sI hydrates. In Fig. 7, the XRD pattern obtained matches perfectly to a typical sII hydrate pattern with space group *Fd3m.*

[0090] Raman spectroscopy is commonly used for hydrate characterization as it is a non-destructive test. Fig. 8 presents the Raman spectra of the obtained methane hydrate in the spectral range of the THF system (400-3500 cm^{-1}). Fig. 9 shows the C-C-C-C stretching vibrations of THF as a single sharp characteristic band around 914 cm^{-1}. This band is typical for THF occupying large cages of sII. While C-O-C stretching of THF is shown in a weak mode at 1031 cm^{-1}, the $-CH_2$ bending of THF is represented by peaks at 1451 cm^{-1}. The sharp signal that appears at 2911 cm^{-1} clearly indicates the occupancy of methane molecules in the small (5^{12}) cages of sII hydrate (Fig. 10).

Experimental results

[0091] The induction times measured for the tested promotors and the blank sample are compared in Fig. 11. All promoters led to shorter induction times, indicating that the kinetics of the methane hydrate formation were improved compared to the blank sample. The non-acidic promotors 13X-Na and Y-54-NH_4 resulted in shorter induction times, the Brønsted acidic promotor Y-54-H together with the surfactant SDS resulted in an even shorter induction time and the Brønsted acidic promotor Y-54-H alone resulted in the shortest induction time, indicating that the kinetics of the methane hydrate formation were best for Y-54-H.

[0092] Without wishing to be bound by theory, it is assumed that while solids like zeolites may accelerate a methane hydrate formation, cations and in particular sodium cations inhibit such a methane hydrate formation. This is in line with the result that the 13X-Na and Y-54-NH_4 samples did not improve the kinetics to an extent as observed for Y-54-H alone and for Y-54-H in the copresence of a surfactant.

[0093] Without wishing to be bound by theory, it is generally assumed that the acidic sites within a solid Brønsted acid selected from aluminosilicates allow for an exchange of cations. That is, cations and in particular sodium cations are taken up by such a solid Brønsted acid from the surrounding aqueous solution when forming methane hydrate, while protons are released into the aqueous solution. In this way, the detrimental impact of the cations on the methane hydrate formation is alleviated and the kinetics of the methane hydrate formation is further improved by use of the solid Brønsted acid as a promoter. The basis for the aqueous solution used for the methane hydrate formation may thus even be sodium-rich seawater, which expands the range of possible applications for the solid Brønsted acid selected from aluminosilicates when used for forming methane hydrates.

[0094] Without wishing to be bound by theory, it is further assumed that the Brønsted acidity of the used solid Brønsted acid selected from aluminosilicates stabilizes the cages of the formed methane hydrates, and that upon release of protons into the surrounding aqueous solution hydronium ions are formed which further improve the kinetics of the methane hydrate formation.

[0095] Without wishing to be bound by theory, it is further assumed that an anionic surfactant bearing a cation, like the sodium cation in SDS, impairs the above-described effect of a solid Brønsted acid in a methane hydrate formation. In line with this assumption, the best results were achieved when the solid Brønsted acid was used in the absence of a surfactant and in particular in the absence of an anionic surfactant like SDS.

[0096] The methane uptakes measured for the tested promotors and the blank sample are compared in Fig. 12. The best results are obtained when the solid Brønsted acid Y-54-H alone was used in the formation of methane hydrate. The solid Brønsted acid allowed for a methane uptake of more than 56 mmol per mol of water. This uptake is above the uptake observed for the blank sample and indicates that the use of the solid Brønsted acid also improved the ability of the overall system to store methane in the form of hydrates. It was further seen that the promotors 13X-Na and Y-54-NH_4 resulted in methane uptakes which were slightly lower than the methane uptake observed for the blank sample. Without wishing to be bound by theory, it is assumed that the cations present in those two promoters impair the methane uptake to some extent. The lowest methane uptake was observed when Y-54-H was used together with SDS, indicating that the presence of a surfactant and in particular the presence of an anionic surfactant like SDS impairs the methane uptake in a methane hydrate formation. Without wishing to be bound by theory, it is assumed that foaming effects lead to such a negative influence of the surfactant.

[0097] The methane conversion measured for the tested promotors and the blank sample are compared in Fig. 13. The trends are naturally the same as seen for the methane uptakes reported in Fig. 12. The conversion of the solid Brønsted acid Y-54-H alone is still better than the conversion of the blank sample. This is not directly apparent from Fig. 13 due to rounded percentages. What is however immediately seen from Fig. 13 is that the solid Brønsted acid led to a conversion of as high as 94%. This high conversion rate is to be seen in the context of the improved kinetics of the solid Brønsted acid as described with reference to Fig. 11. One of the major challenges for an industrialization of methane hydrates for energy storage is the slow kinetics of their formation. A particular target of a hydrate kinetic promoter is to get the highest gas conversion in a shorter time. As seen in Fig. 11, the inventive use of a solid Brønsted acid selected from aluminosilicates significantly reduces the induction time and thus improves the kinetics of the methane hydrate formation, while the methane conversion of 94% shown in Fig. 13 demonstrates that simultaneously an enhanced storage capacity can be achieved.

[0098] At the same time, the Examples presented herein show that relaxed conditions like a pressure of as low as 6 MPa and a temperature of as high as 283.2 K are sufficient for a successful methane hydrate formation when a solid Brønsted acid selected from aluminosilicates is used as a promoter of the formation.

[0099] Overall, it is seen that the use of a solid Brønsted acid selected from aluminosilicates for forming methane hydrate according to the invention accelerates the methane hydrate formation and leads to a high conversion of methane into methane hydrate. The use also allows for an improved separation of methane from other gases, while less energy, lesser operational expenditures and lesser capital expenditures are needed. Analogous conclusions can be drawn for the inventive methods, methane hydrates and methane hydrate forming compositions.

Claims

1. Use of a solid Brønsted acid selected from aluminosilicates for forming methane hydrate.

2. The use according to claim 1, wherein the solid Brønsted acid has a concentration of Brønsted acidic sites of ≥ 10 μmol/g .

3. The use according to at least one of the preceding claims, wherein the solid Brønsted acid is made of a zeolite having a ratio of $Si/Al > 2$, preferably of $2.5 \leq Si/Al \leq 100$.

4. The use according to at least one of the preceding claims, wherein the solid Brønsted acid is a zeolite in which at least 10% of all Al-sites are in H-form.

5. The use according to at least one of the preceding claims, wherein the solid Brønsted acid is a FAU-type zeolite, an MFI-type zeolite, a CHA-type zeolite or an MOR-type zeolite, preferably a FAU-type zeolite.

6. The use according to at least one of the preceding claims, wherein the methane hydrate is formed in the presence of a hydrate former different from water, which is preferably selected from tetrahydrofuran, cyclopentane, tetra-n-butyl ammonium bromide, propylene oxide, 1, 4-dioxane and cyclooctane.

7. The use according to at least one of the preceding claims, wherein the methane hydrate is formed at an absolute pressure below 8 MPa and/or at a temperature above 280 K.

8. The use according to at least one of the preceding claims, wherein the methane hydrate is formed in the absence of sodium dodecyl sulfate, preferably in the absence of a surfactant.

9. The use of a solid Brønsted acid according to at least one of the preceding claims, wherein the solid Brønsted acid has a concentration of Brønsted acidic sites of ≥ 100 to ≤ 2000 μmol/g, wherein the solid Brønsted acid is a Y-type zeolite having a ratio of $2 < Si/AL < 100$, and wherein the methane hydrate is formed in the presence of tetrahydrofuran.

10. A method of forming a methane hydrate, comprising the steps:

i) providing a solid Brønsted acid selected from aluminosilicates, and
ii) converting a mixture comprising water and methane into a methane hydrate in the presence of the solid Brønsted acid provided in step i).

11. The method of claim 10, wherein prior to step i), an aluminosilicate having no Brønsted acidic sites is converted into the solid Brønsted acid provided in step i).

12. A methane hydrate obtainable by the use according to any of claims 1 to 9, or obtainable by the method according to claim 10 or 11.

13. The methane hydrate according to claim 12, which is a sII hydrate which preferably comprises tetrahydrofuran.

14. A methane hydrate forming composition comprising methane, water and a solid Brønsted acid selected from aluminosilicates.

15. The composition according to claim 14, which contains the solid Brønsted acid in an amount of ≥ 0.001 wt.% to $\leq$

2 wt.%, based on the total weight of the composition.

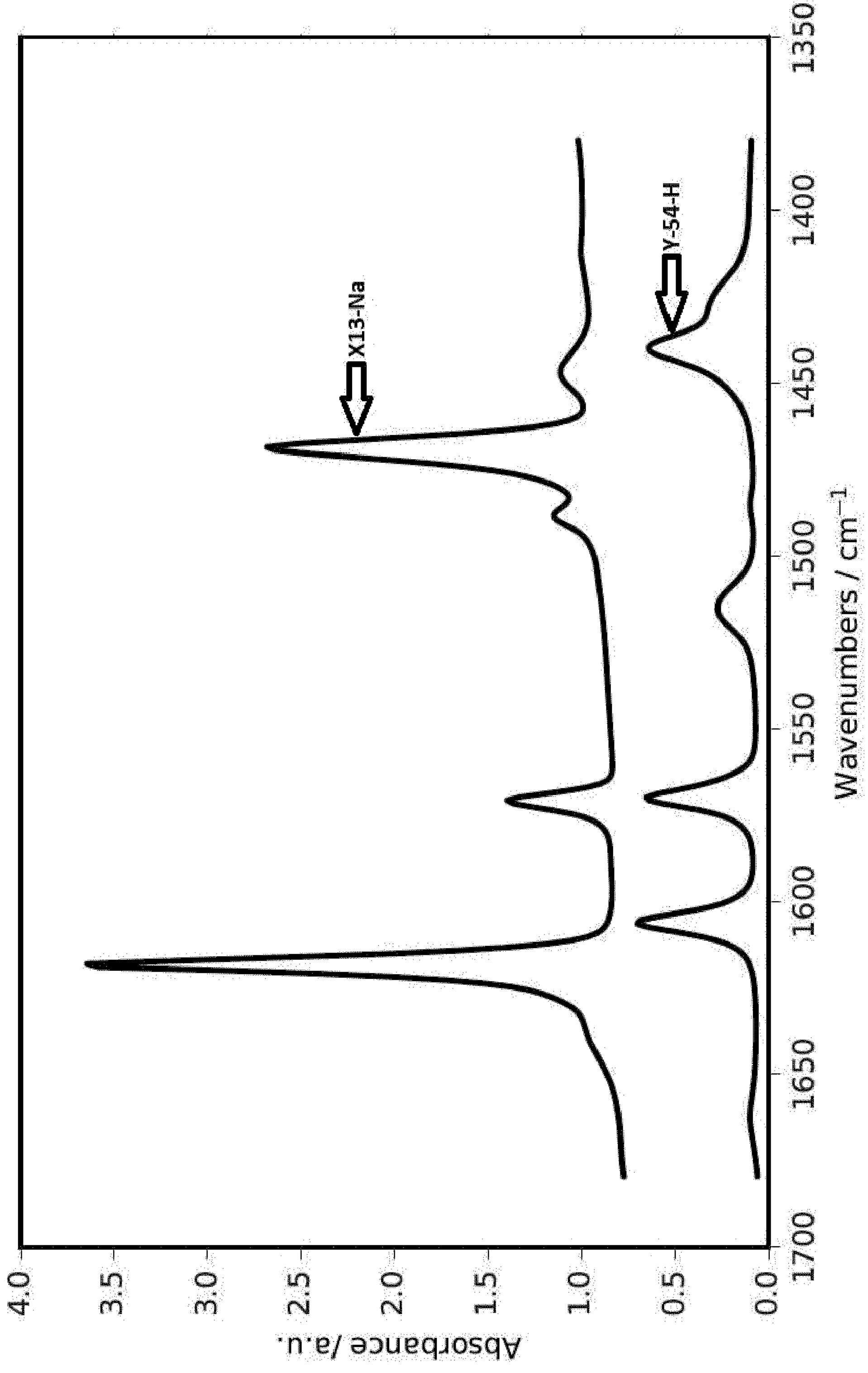
X13-Na
Y-54-H
Absorbance /a.u.
Wavenumbers / cm^{-1}
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1700
1650
1600
1550
1500
1450
1400
1350

Fig. 1

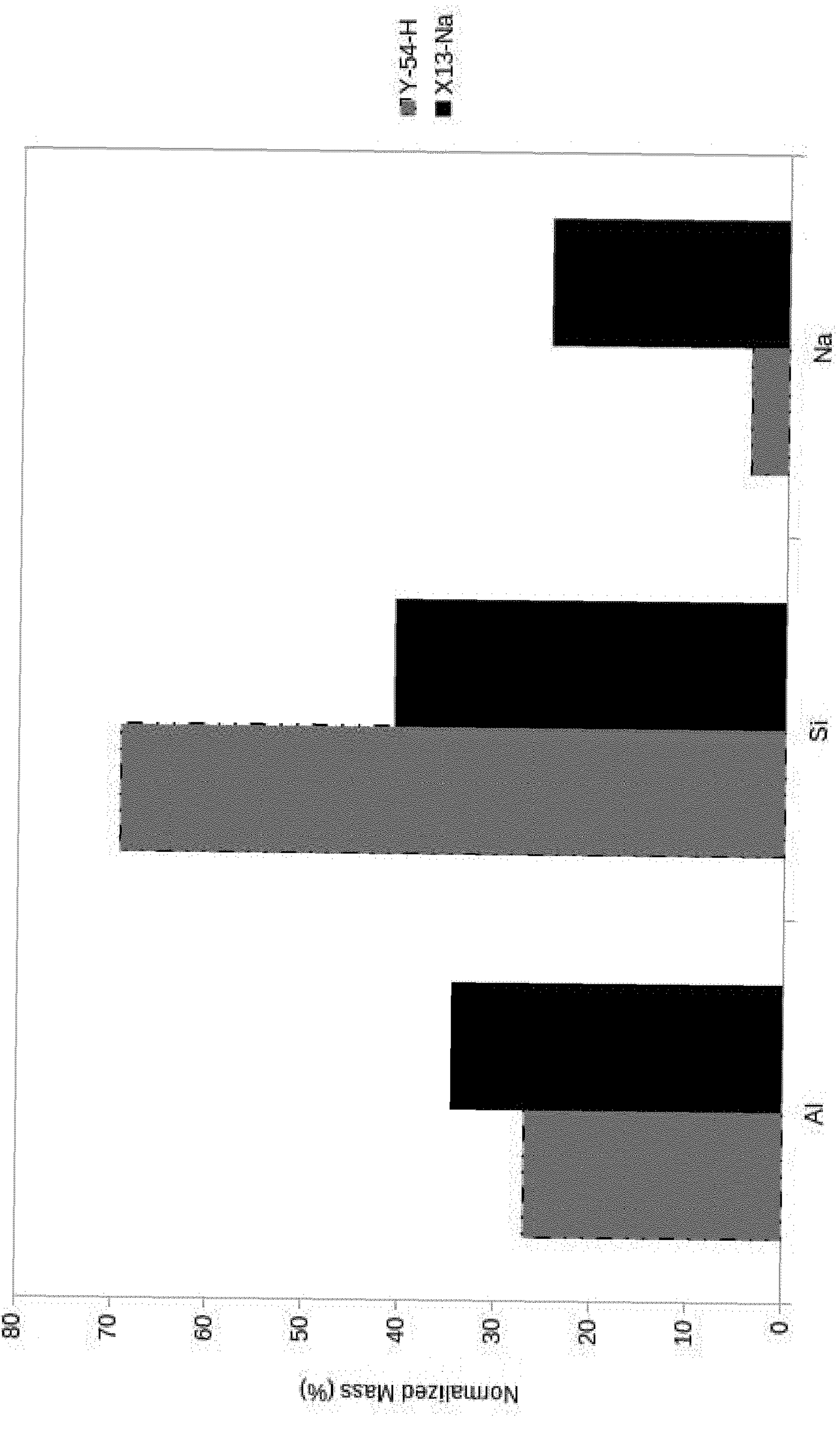

Fig. 2

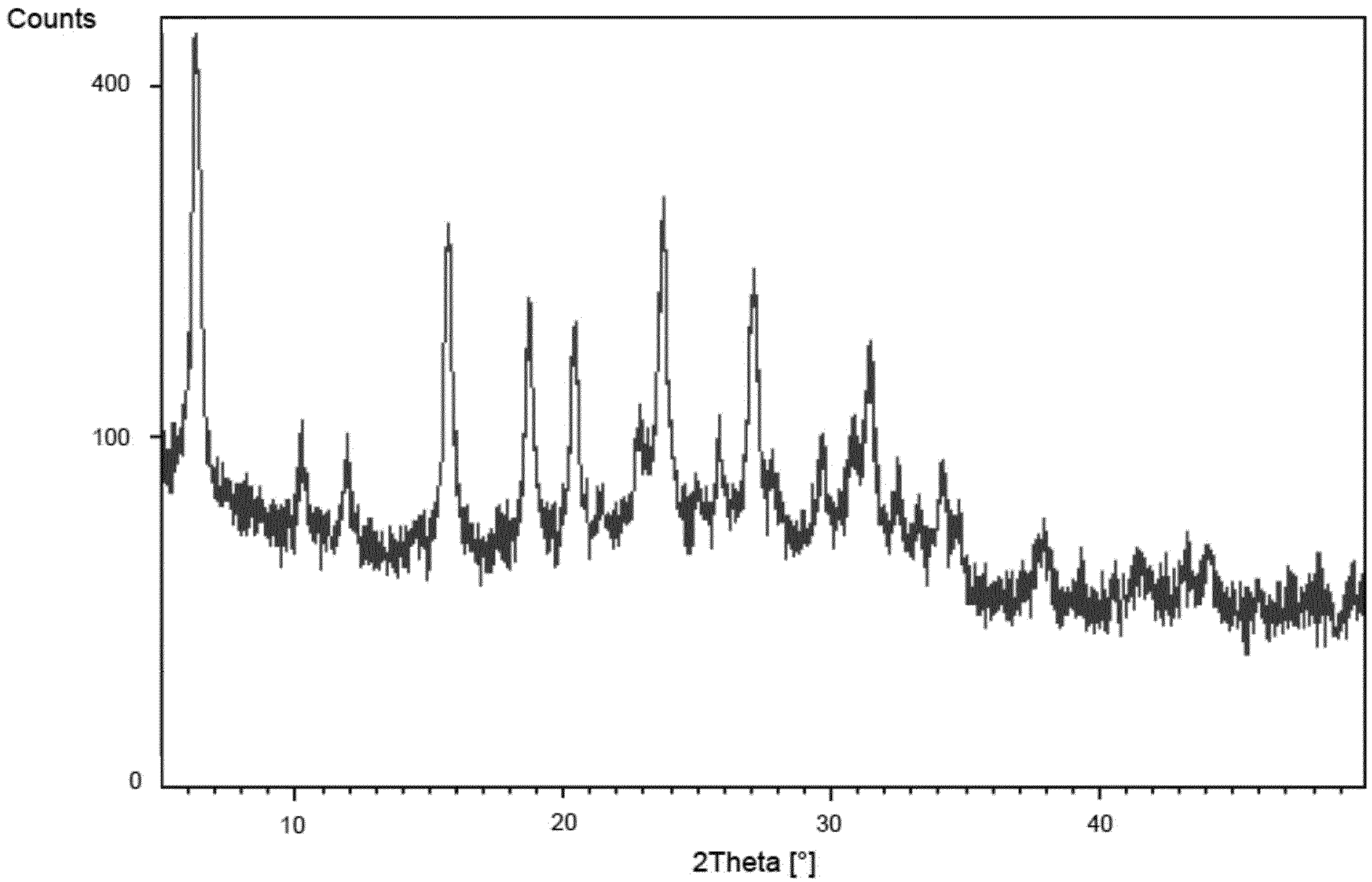

Fig. 3

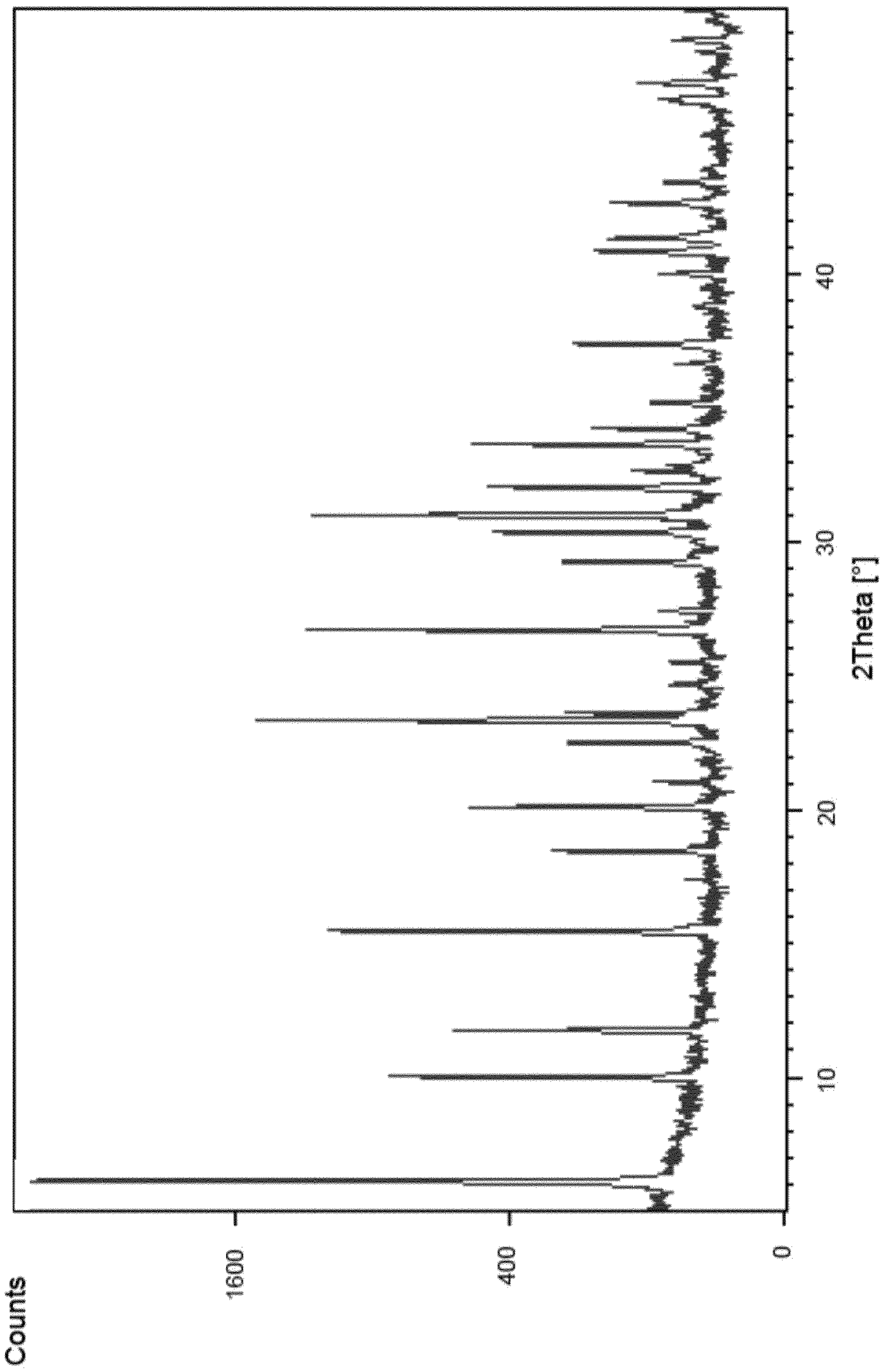

Fig. 4

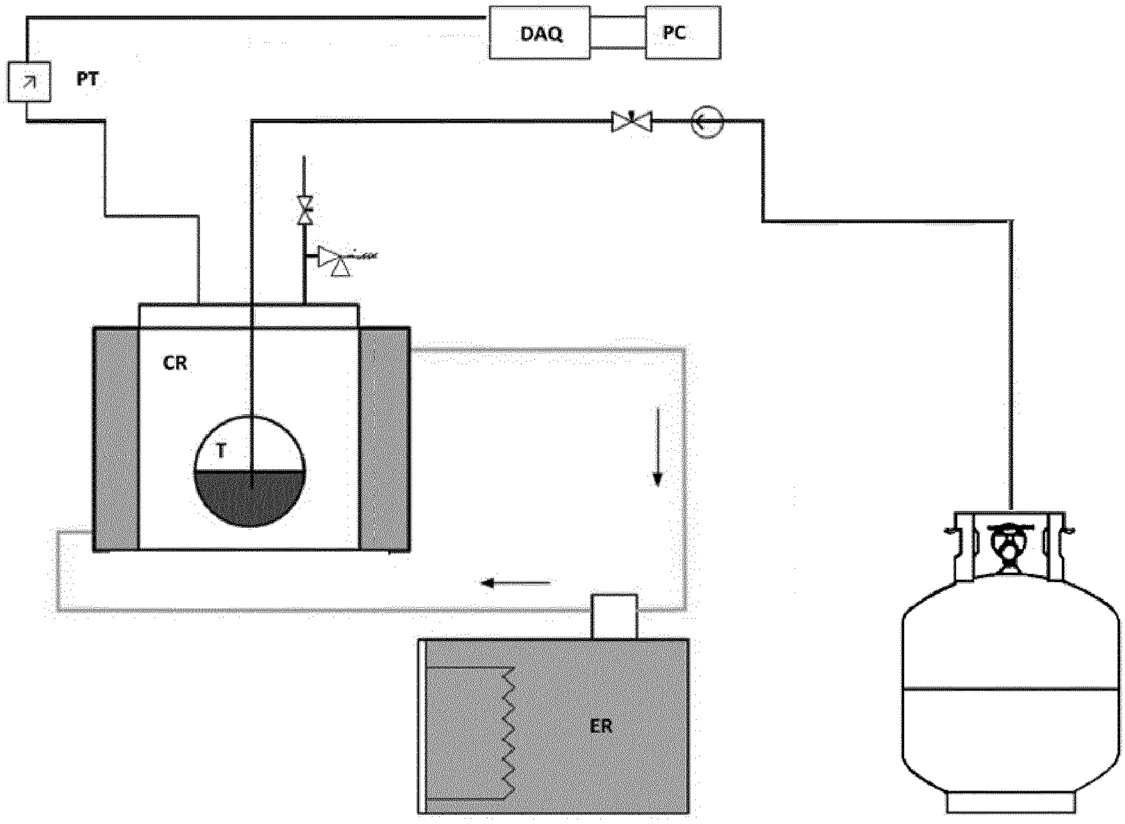

Fig. 5

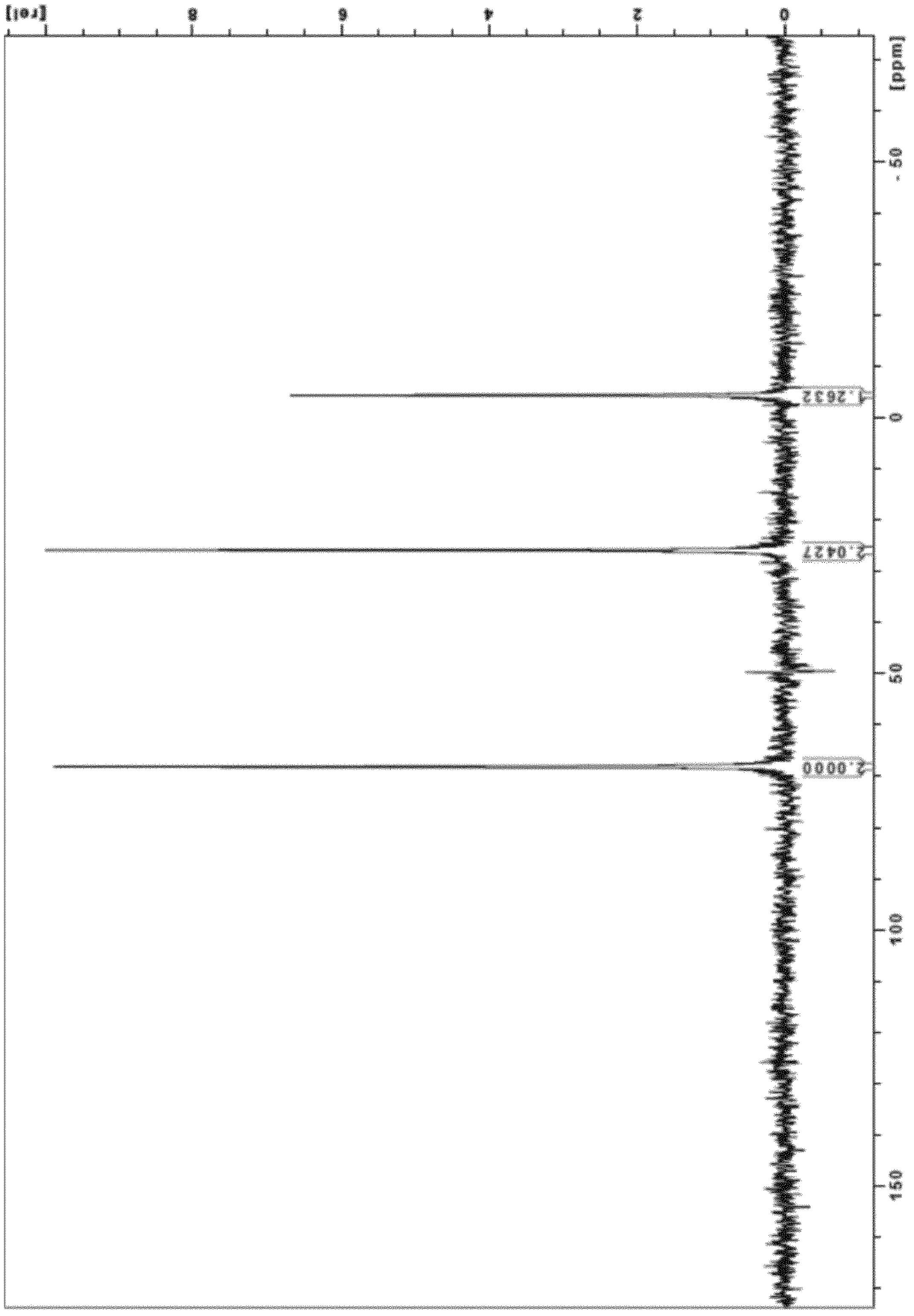

Fig. 6

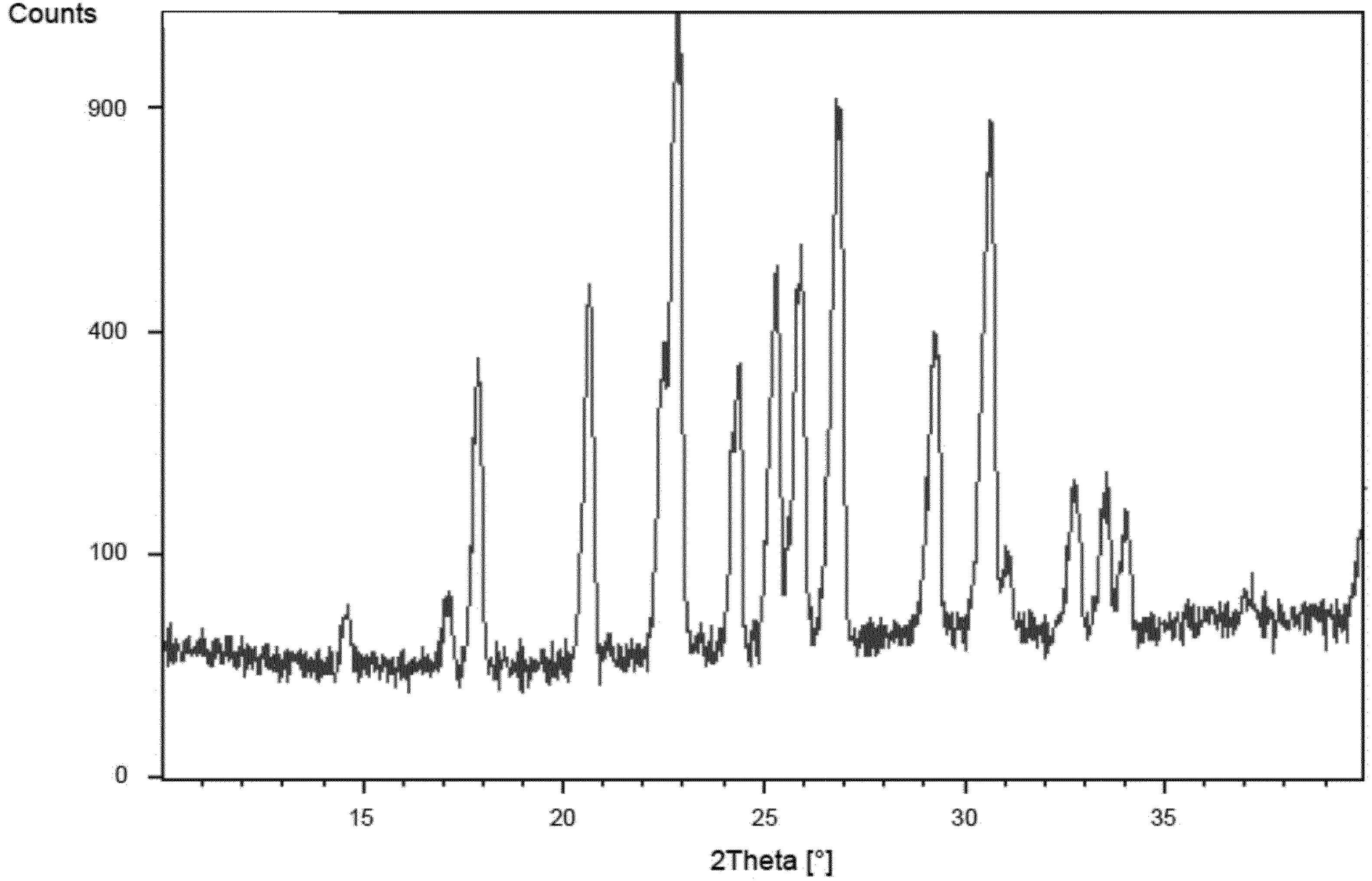

Fig. 7

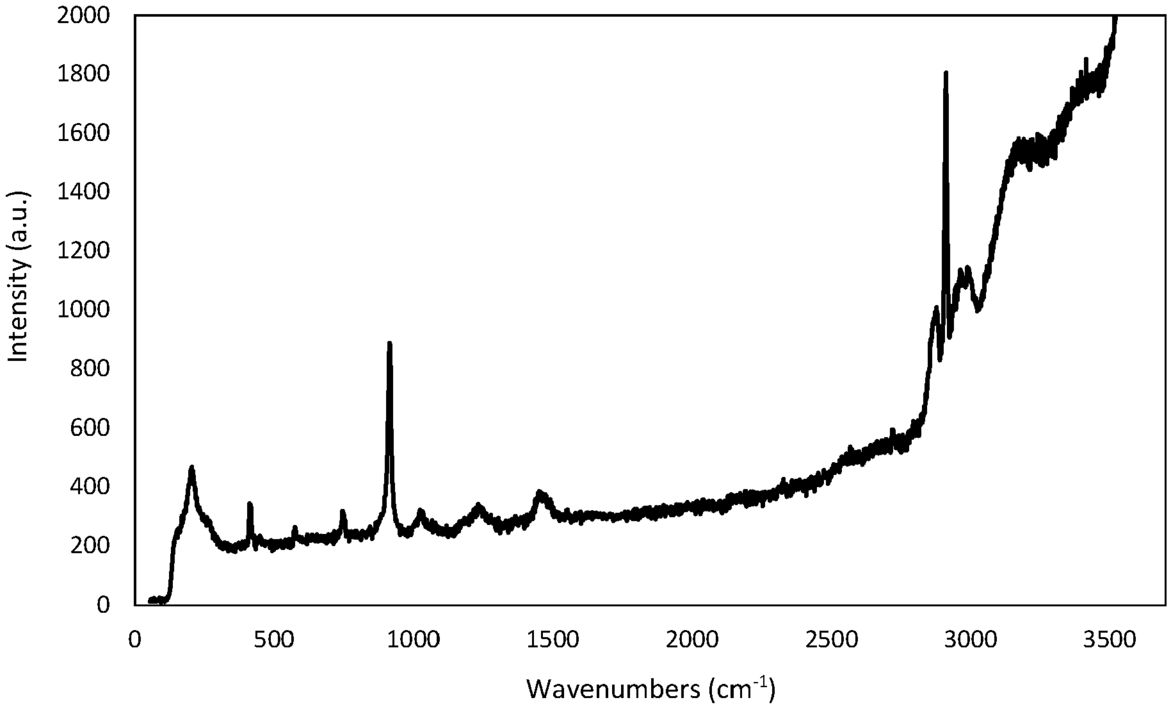

Fig. 8

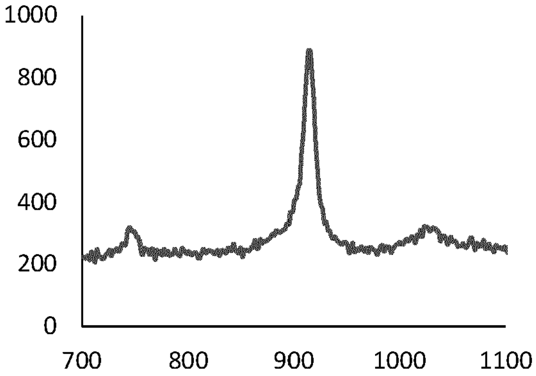

Fig. 9

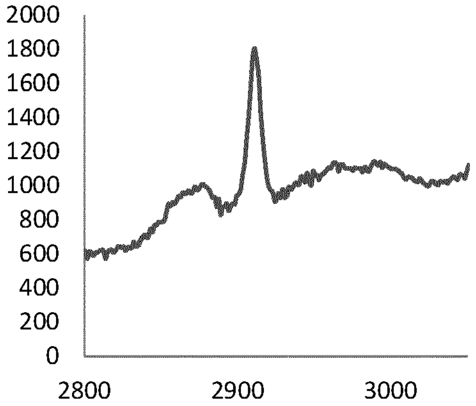

Fig. 10

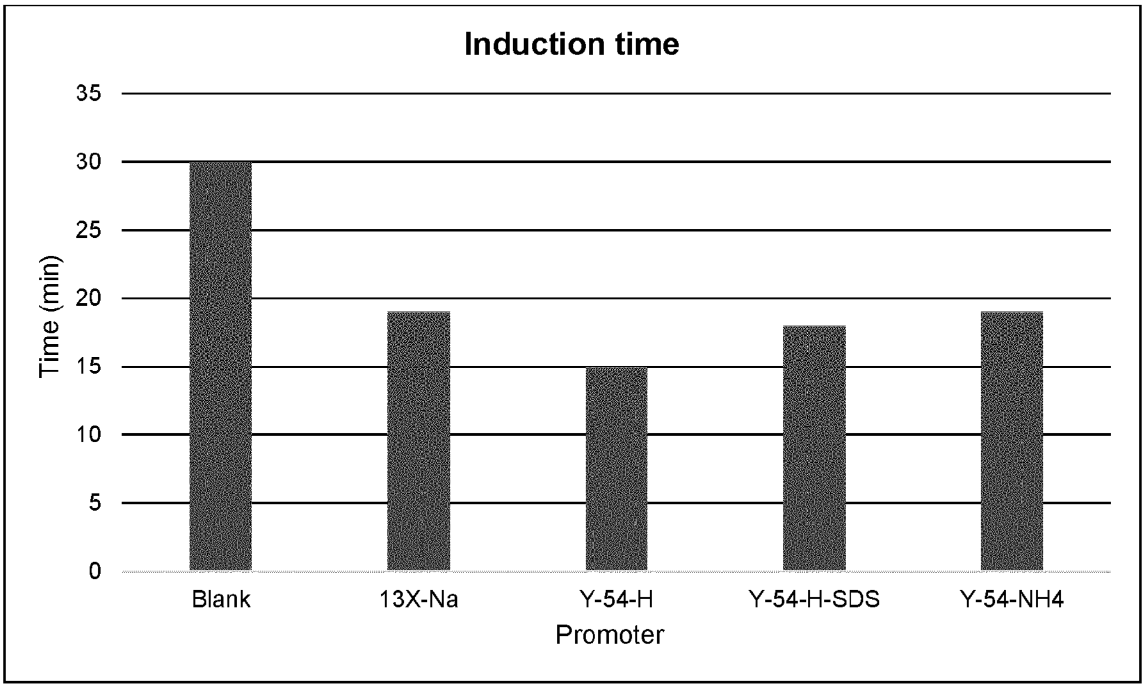
Induction time
35
30
25
20
15
10
5
0
Time (min)
Blank
13X-Na
Y-54-H
Y-54-H-SDS
Y-54-NH4
Promoter

Fig. 11

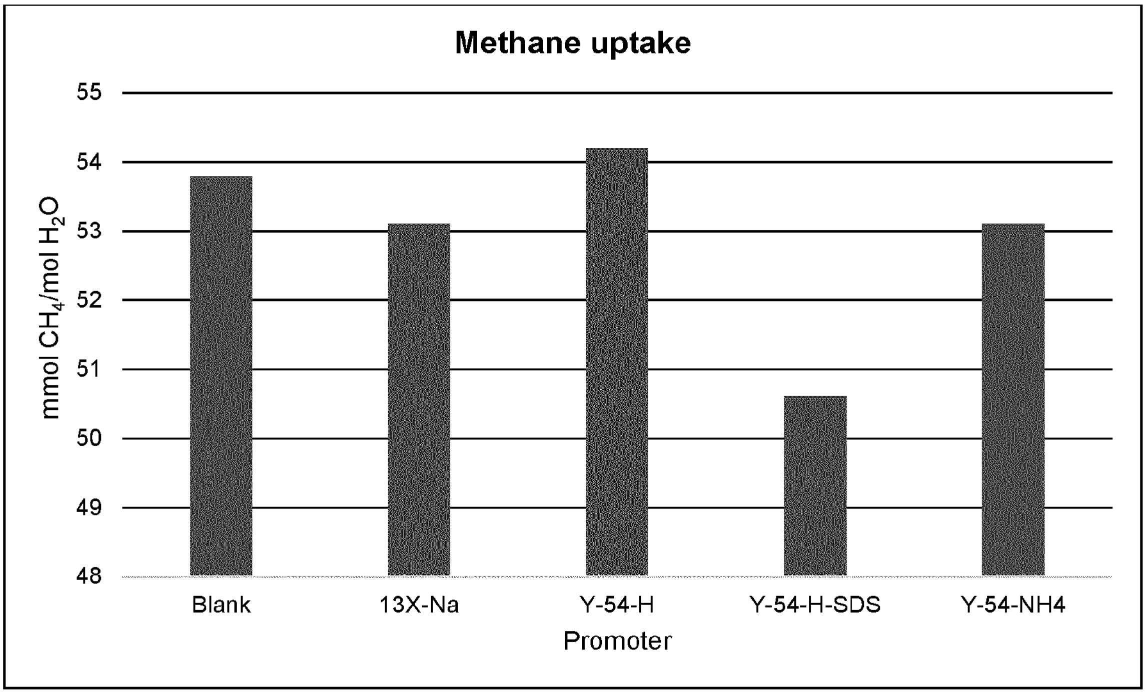
Methane uptake
55
54
53
52
51
50
49
48
mmol CH_4/mol H_2O
Blank
13X-Na
Y-54-H
Y-54-H-SDS
Y-54-NH4
Promoter

Fig. 12

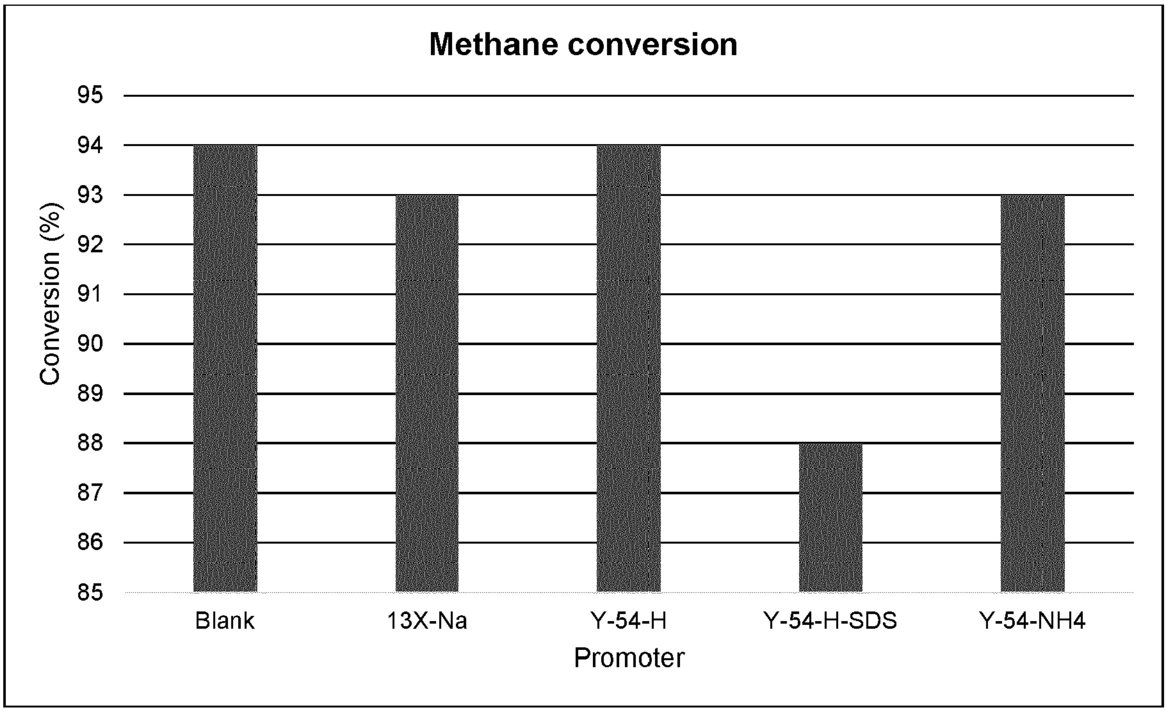
Methane conversion
95
94
93
92
91
90
89
88
87
86
85
Conversion (%)
Blank
13X-Na
Y-54-H
Y-54-H-SDS
Y-54-NH4
Promoter

Fig. 13

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 22 15 6772

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DENNING SHURRAYA ET AL: "Promoting Methane Hydrate Formation for Natural Gas Storage over Chabazite Zeolites", ACS APPLIED ENERGY MATERIALS, vol. 4, no. 12, 15 December 2021 (2021-12-15), pages 13420-13424, XP55937520, ISSN: 2574-0962, DOI: 10.1021/acsaem.1c02902 Retrieved from the Internet: URL:https://pubs.acs.org/doi/pdf/10.1021/acsaem.1c02902>	1,5,7,8, 10,12-15	INV. C10L3/10
A	* page 13421 - page 13423 * -----	2-4,6,9	
X,D	ZHAO YANGSHENG ET AL: "Semi-clathrate hydrate process of methane in porous media-microporous materials of 5A-type zeolites", FUEL, IPC SIENCE AND TECHNOLOGY PRESS , GUILDFORD, GB, vol. 220, 8 February 2018 (2018-02-08), pages 185-191, XP085369306, ISSN: 0016-2361, DOI: 10.1016/J.FUEL.2018.01.067	12,13	
A	* page 187, paragraph 3 - page 190, paragraph 4 * ----- -/--	1-11,14, 15	

TECHNICAL FIELDS SEARCHED (IPC)
C10L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	4 July 2022	Pöllmann, Klaus

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 22 15 6772

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	**Chen J. ET AL: "Understanding The Brønsted Acidity of Sapo-5, Sapo-17, Sapo-18 and SAPO-34 and Their Catalytic Performance for Methanol Conversion to Hydrocarbons"** **In: "Zeolites and related materials: Trends, targets and challenges",** **1 January 1994 (1994-01-01), Elsevier BV, NL, XP055937813,** **ISSN: 0167-2991** **vol. 84, pages 1731-1738, DOI: 10.1016/S0167-2991(08)63726-X,** **Retrieved from the Internet:** **URL:http://dx.doi.org/10.1016/S0167-2991(08)63726-X>** *** abstract *** -----	**1-15**	
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	**4 July 2022**	**Pöllmann, Klaus**

2

EPO FORM 1503 03.82 (P04C01)

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

REFERENCES CITED IN THE DESCRIPTION

Non-patent literature cited in the description

- **ZANG et al.** *Sci China Ser B-Chem,* September 2008, vol. 51 (9), 893-900 **[0005]**
- **ZHAO et al.** *Fuel,* 2018, vol. 220, 185-191 **[0005]**
- **JAVIDANI et al.** *Journal of Molecular Liquids,* 2020, vol. 316, 113872 **[0005]**
- **ZANG et al.** *Chin. J. Chem. Eng.,* 2009, vol. 17 (5), 854-859 **[0006]**
- **KIM et al.** *Int. J. Energy Res.,* 2015, vol. 39, 26-32 **[0006]**
- **ANDRES-GARCIA et al.** *Chemical Engineering Journal,* 2019, vol. 360, 569-576 **[0007]**
- **S. DENNING et al.** *ACS Appl. Energy Mater.,* 2021, vol. 4, 13420-13424 **[0008]**
- **HO-VAN et al.** Experimental measurement and thermodynamic modeling of cyclopentane hydrates with NaCl, KCl, CaCl2, or NaCl-KCl present. *AIChE J,* 2018, vol. 64, 2207-2218 **[0075]**
- **NAJIBI et al.** *Journal of Natural Gas Science and Engineering,* 2015, vol. 23, 315-323 **[0087]**