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(54) **Title:** ANHYDROUS, AMORPHOUS AND POROUS MAGNESIUM CARBONATES AND METHODS OF PRODUCTION THEREOF

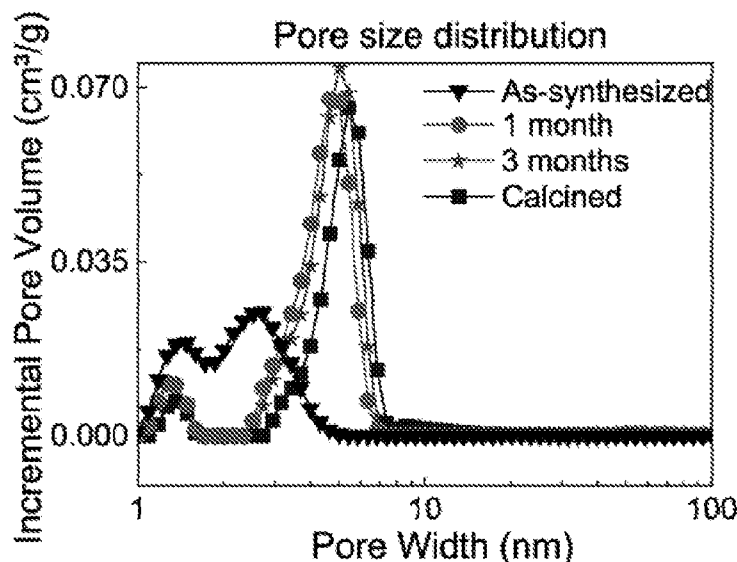


Figure 31.

(57) **Abstract:** An X-ray amorphous magnesium carbonate is disclosed that is characterized by a cumulative pore volume of pores with a diameter smaller than 10 nm of at least 0.018 cm<sup>3</sup>/g, and a specific surface areas of at least 60 m<sup>2</sup>/g. The X-ray amorphous magnesium carbonate is produced by reacting an inorganic magnesium compound with alcohol in a CO<sub>2</sub> atmosphere. The X-ray amorphous magnesium carbonate can be a powder or a pellet and acts as a desiccant in, for example, production of food, chemicals or pharmaceuticals.



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**ANHYDROUS, AMORPHOUS AND POROUS MAGNESIUM CARBONATES AND  
METHODS OF PRODUCTION THEREOF**

**RELATED APPLICATION DATA**

- 5 This application is based on and claims priority to U.S. Provisional Patent Application No. 61/734,144, filed December 6, 2012, the entire contents of which are incorporated herein by reference.

**FIELD OF INVENTION**

- 10 The present invention relates to an amorphous, anhydrous, micro porous magnesium carbonate with large specific surface areas and extraordinary moisture sorption properties and to a method of forming such. The invention further relates to, but is not limited to: dehumidifiers, moisture control, vacuum insulation panel and thermochemical energy storage materials, delivery or carrier systems for therapeutic and cosmetic or volatile agents, odour  
15 control, sanitation after fire or fire retardants, as well as to materials for collection of toxic waste, chemicals or oil spill and to materials for pest control and for protection of crops and food stuff.

**BACKGROUND OF THE INVENTION**

- 20 In the discussion that follows, reference is made to certain structures and/or methods. However, the following references should not be construed as an admission that these structures and/or methods constitute prior art. Applicant expressly reserves the right to demonstrate that such structures and/or methods do not qualify as prior art against the present invention.

Magnesium is the eighth most abundant element in the earth's crust and essential to most living species. It can form several forms of hydrated carbonates such as nesquehonite ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ), and lansfordite ( $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ ), a number of basic carbonates such as hydromagnesite ( $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ), and dypingite ( $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ ) as well as the anhydrous and rarely encountered magnesite ( $\text{MgCO}_3$ ). The various forms of magnesium carbonate are all industrially important materials and for example used in pharmaceuticals as antacids, adsorbents and diluents in direct compression tablets. They are also found in cosmetics thanks to their mild astringent properties which help to smoothen and soften skin, and have found their applications in dusting powders, face masks as well as in toothpastes. In addition, high purity magnesium carbonates are useful desiccants, for instance, as an additive in table salt to keep it free flowing or as a drying agent for hands to improve the grip, e.g. for rock climbing, gymnastics, and weight lifting.

Commercial (crystalline) analogues of magnesium carbonates typically show specific surface areas (SSAs) of about  $4\text{--}18 \text{ m}^2 \text{ g}^{-1}$ . For previously reported X-ray amorphous magnesium carbonates produced by thermal decomposition of hydrated magnesium carbonates forms, the highest SSA found in the literature is  $\sim 50 \text{ m}^2 \text{ g}^{-1}$ .

For many geologists, the anhydrous (native) magnesite is a conspicuous rock with unclear genesis. Although magnesium carbonates are abundant in nature in the form of minor traces in most geological structures, magnesium carbonate rarely exists as a monomineralic magnesite in economically viable deposits. In fact, there are virtually only two types of magnesite deposits in the world: the sparry magnesite of Vietsch type, which constitutes 90% of world's reserves and forms nearly monomineralic lenses within marine platform sediments, and the less common but highly valued Kraubath type magnesite of superior quality. The Kraubath type consists of veins (300-400 meter deep) and stockworks (80 meter deep) of cryptocrystalline "bone" magnesite, also sometimes referred to as gel-magnesite. It commonly

occurs together with ultramafic rock structures such as serpentine  $((\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4)$  and olivine  $((\text{Mg,Fe})_2\text{SiO}_4)$  minerals. The formation of Kraubath type magnesite is suggested to occur through a so-called epigenetic-hydrothermal route, wherein hydrothermal fluids of moderate temperature and low salinity carrying  $\text{CO}_2$  interact with ultramafic rocks. Most of the silica and iron derived from the decomposition of ultramafic rocks are carried to the surface whereas the veins of magnesite precipitate *in situ* as a gel.

In nature, magnesium carbonate occurs in two physical forms; as macrocrystalline or cryptocrystalline magnesite. The cryptocrystalline form is also sometimes referred to as amorphous or gel magnesite by geologists, however, it should be stressed that this does not imply that it is X-ray amorphous, merely that the size of the crystallites are too small to be observe with a light microscope. Hereinafter the term amorphous should be interpreted to mean X-ray amorphous.

X-ray amorphous magnesite has been observed upon thermal decomposition of crystalline hydrated magnesium carbonates occurring at temperatures of the order of  $300\text{ }^\circ\text{C}$  or higher. Such magnesites are, however, not stable upon long term storage in humid atmosphere as it has been shown that the carbonate bond is weakened during rehydration. This weakening is evident by the fact that the decarbonation peak in differential Thermogravimetric measurement (dTGA) curves at about  $350\text{ }^\circ\text{C}$  or above develops a shoulder and/or splits into two or more peaks and also shifts towards lower temperatures.

Interestingly, magnesite has stirred problems not only for the geologists but also for the chemists. Anhydrous  $\text{MgCO}_3$  can easily be produced at elevated temperatures. However, numerous authors, have described unsuccessful attempts to precipitate anhydrous magnesium carbonate from a magnesium bicarbonate solution kept at room temperature and under atmospheric pressure. Instead, hydrated magnesium carbonates or one of the more complex

basic magnesium carbonates precipitated under such conditions leading to what has been branded as "the magnesite problem".

In 1999, successful attempts of making crystalline magnesite at 400 °C and atmospheric pressure was presented by using a suspension of artificial sea-water with calcium carbonate and urea through which CO<sub>2</sub> was bubbled followed by dissolution and titration with dilute ammonia during which carbonate precipitated. The precipitate was characterized as crystalline magnesite using X-ray diffraction, and traces of aragonite (CaCO<sub>3</sub>) and possibly calcite (CaCO<sub>3</sub>) were noted in the diffractogram. The experiment has since been repeated and the precipitates consisted of magnesite with traces of aragonite (CaCO<sub>3</sub>) and dypingite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)·5H<sub>2</sub>O). In both of the experiments magnesite was formed after 14 dissolution-precipitation cycles.

It should be mentioned that magnesium carbonate was attempted to be synthesized also in non-aqueous solvents during the early 1900's. However, it was concluded that magnesium carbonate cannot be obtained by passing CO<sub>2</sub> gas through methanolic suspensions of MgO due to the more likely formation of magnesium dimethyl carbonate Mg(OCO)(OCH<sub>3</sub>)<sub>2</sub>.

Subsequent studies only reiterated the assumption that MgO preferentially forms complex dimethyl carbonates when reacted with CO<sub>2</sub> in methanol. This conclusion was especially peculiar since carbonates of other rare earth metals, such as those of Ca, Ba, and Sr, can be readily produced by passing CO<sub>2</sub> gas through alcoholic suspensions of their respective oxides.

In view of the above-mentioned industrial applications of magnesium carbonates and their non-toxic properties, further improvements in the magnesium carbonates and their production methods are desirable to allow for expanded use of magnesium carbonates in various applications. As well, introduction of a new class of magnesium carbonate containing materials with structural and functional properties that have currently not been found in

previously disclosed magnesium carbonate containing materials are foreseen to open up for new industrial applications and for improved functionality in already existing applications. To become industrially attractive, areas of improvements include water sorption properties, porosity, specific surface area, long term stability of the material and the cost of production.

- 5 There are, to our knowledge, no prior art disclosing a magnesium carbonate material containing micro and/or meso pores, neither among the reports describing crystalline magnesium carbonates nor the X-ray amorphous ones produced by thermal decomposition. A nitrogen sorption analysis performed on, e.g., hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ ), which is the pharmaceutical grade of magnesium carbonate, reveals a material with no
- 10 porosity in the micro pore range and with some meso pores between, but not inside, the powder particles, as will become evident in the drawings and examples that follows.

Magnesium carbonates are well known for their desiccant properties in applications like those mentioned above, e.g., for keeping table salt free flowing in humid climates and as gripping agents in rock climbing. Existing magnesium carbonate majorly adsorbs moisture around or

15 above 70 % relative humidity (RH) at room temperature and are not known to be good moisture adsorbents at low RHs.

The stability of presently known amorphous and anhydrous magnesium carbonates, i.e. those produced by thermal decomposition of crystalline hydrated magnesium carbonates, are known to be limited upon storage in humid environments. The carbonate bond of such materials

20 usually weakens after only 2 weeks of storage in 100 % humidity, preventing a regeneration of the materials original structure and properties.

## SUMMARY OF THE INVENTION

It is an object of the present invention to provide a novel group of magnesium carbonate based materials with improved properties with regards to, for example, surface area, micro and meso pore volume, moisture sorption properties and regeneration properties as well as storage stability as compared to other carbonates as well as to other classes of materials used for, e.g., moisture sorption and drug delivery, as well as other applications exemplified herein. It is a further object to provide methods of producing such magnesium carbonate based materials, which are industrially feasible.

Herein micro pores, refers to pores with a diameter less than 10 nm and meso pores refers to pores with diameters between 10 and 100 nm, instead of the traditionally used range of 2-50 nm. Accordingly, micro porous refers to a material comprising micro pores with a diameter less than 10 nm and meso porous refers to a material comprising meso pores with a diameter between 10 nm and 100 nm.

Surprisingly, we have found that anhydrous, amorphous, micro porous, high specific surface area magnesium carbonate with unique moisture sorption properties at low RHs can be produced at low temperatures from a Mg-containing precursor, like MgO, in organic solvents. The magnesium carbonate produced can be either in the form of suspension, gel or powder. The produced magnesium carbonate has a surface area much larger than that reported for any other magnesium carbonate material and comprises a substantial portion of micro pores, i.e. a cumulative volume of pores with a diameter smaller than 10 nm in the range 0.018 - 3 cm<sup>3</sup>/g. The novel material is stable upon storage at high RHs for prolonged time periods, in contrast to earlier described amorphous magnesium carbonate materials. Further, we have also found that the produced magnesium carbonate has excellent moisture sorption properties, especially at low RHs, which are highly favorable in a number of industrial applications. These and other advantages of the material are described in detail below. The introduction of a new class



of magnesium carbonate containing materials with structural and functional properties that have currently not been found in previously disclosed magnesium carbonate containing materials are foreseen to open up new industrial applications and improved functionality in already existing applications.

- 5 The magnesium carbonate according to the invention is X-ray amorphous, anhydrous, exhibits a cumulative volume of pores with a diameter smaller than 10 nm of at least 0.018 cm<sup>3</sup>/g, preferably of at least 0.4 cm<sup>3</sup>/g, and even more preferably of at least 0.8 cm<sup>3</sup>/g, and a cumulative volume of pores with a diameter smaller than 10 nm up to 1.5 cm<sup>3</sup>/g, or more preferably up to 2 cm<sup>3</sup>/g or most preferably up to 3 cm<sup>3</sup>/g. As appreciated by the skilled  
10 person, the unique distribution of micro and meso pores according to the present invention can be described with other parameters and can be based on other types of measurements than described herein.

- Such pore volume should be determined by Density Functional Theory (DFT) analysis of nitrogen sorption isotherms, wherein the pore size distribution is derived from the nitrogen  
15 isotherm using the DFT method assuming a slit-shaped pore model. The magnesium carbonate according to the invention further exhibits a specific surface areas (SSAs) of at least 60 m<sup>2</sup>/g, preferably of at least 100 m<sup>2</sup>/g, more preferably of at least 240 m<sup>2</sup>/g, even more preferably of at least 350 m<sup>2</sup>/g, most preferably of at least 600 m<sup>2</sup>/g, and a SSA up to 400 m<sup>2</sup>/g, preferably up to 800 m<sup>2</sup>/g, more preferably up to 1000 m<sup>2</sup>/g, even more preferably up to  
20 1200 m<sup>2</sup>/g and most preferably up to 1500 m<sup>2</sup>/g. The specific surface area can be determined from a BET analysis of nitrogen adsorption isotherms.

The method according to the invention of producing the high SSA, porous, amorphous and anhydrous magnesium carbonate, comprises reacting an inorganic magnesium compound, for example MgO, with alcohol in a CO<sub>2</sub> atmosphere. The pressure should preferably be 1-3 bar,

and the temperature 40 °C to boiling temperature of the liquid. The method may be realized by the steps:

**[Step 1]** Mixing a Mg-containing precursor and an alcohol-containing liquid in a reactor,

5 - the mixing is preferable performed under continuous stirring and the consistency of the mixture is preferably of liquid character. During this step, the ingredients in the mixture react to form one or several intermediates that later can interact with CO<sub>2</sub>.

10 - the mixture is preferably heated in order to facilitate reactions between the ingredients in the mixture. Temperatures between 40°C and boiling temperature of the liquid are preferable for the reaction to occur, however lower temperatures down to the freezing temperature of the liquid is enough for a less complete reaction.

- typically about 3h to 24h at 50°C for liquid volumes of 100 to 3000ml.

15

**[Step 2]** Reacting the mixture with CO<sub>2</sub>. In this step, the intermediate products formed during step 1 interact with CO<sub>2</sub> to form one or several types of carbonated intermediate products.

20 -this step can be performed at temperatures ranging from the freezing temperature to the boiling temperature of the liquid, and at CO<sub>2</sub> pressures ranging from 0.001 to 200bar above atmospheric pressure. However, temperatures below 30°C and pressures below 5bar are beneficial for carbonation of the intermediate products.

25 -during this step, the carbonated intermediate products can form a gel in the reactor, typically this occurs after 4-6 days if the CO<sub>2</sub> pressure is 1 bar and the temperature is 20 °C during step 2.

[Step 3] Solidification and drying of the material.

-the liquid or gel formed in the reactor during step 2 is dried in order to obtain a solid material and the carbonated intermediate products formed during step 2 are transformed into anhydrous magnesium carbonate.

-temperatures between 60 °C and 300 °C.

- depending on the intermediates formed during step 1 and 2, presence of water during the step can facilitate the transformation to magnesium carbonate via hydrolysis.

- the drying and solidification process in may include techniques such as spray drying or oven drying.

Thanks to the present invention it is possible to provide an amorphous, anhydrous, micro porous and high surface area magnesium carbonate which is stable upon storage for months or longer, at room temperature and relative humidity at least above 60%. The novel material exhibit extraordinary moisture sorption properties, especially at low RHs, and is comparable, or even superior, to those of hydrophilic zeolites, e.g. zeolite Y ( $600 \text{ m}^2 \text{ g}^{-1}$ , silica/alumina ratio 5.2:1) and also superior to those of commonly used dessicants, e.g. fumed silica (Aerosil) or crystalline hydromagnesite. As measured using an ASAP 2020 from Micromeritics equipped with a water vapor source, the novel magnesium carbonate material adsorbs more than 0.6 mmol water /g material, preferably more than 0.7 mmol water /g material, even more preferably more than 1 mmol or 2 mmol water / g material, most preferably more than 3 mmol water /g material at an RH of 3% at room temperature. It adsorbs more than 1.5 mmol water /g material, preferably more than 1.7 mmol water /g material, even more preferable more than 2 mmol water /g material, most preferably more

than 4 or 5 mmol water /g material at an RH of 10% at room temperature and adsorbs more than 10 mmol water /g material, more preferably more than 14 mmol water /g material, most preferably more than 20 mmol water /g material at an RH of 90% at room temperature.. Also the moisture retention ability and regeneration properties are extraordinary; experiments have

5 verified that the novel magnesium carbonate material retains more than 80 wt% of the adsorbed moisture when the RH is lowered from 90% to 5% during a water vapor desorption analysis performed at room temperature. Experiments have further verified that the novel magnesium carbonate material retains more than 90 wt% of the adsorbed moisture when the RH is lowered from 90% to 20% during a water vapor desorption analysis performed at room

10 temperature. Additional experiments have shown that the moisture sorption properties of the novel magnesium carbonate material can be regenerated after storing the material at RH higher than 90% RH for at least 7 days at room temperature by drying the material at only 95 °C during less than 24 hours.

The amorphous, anhydrous, micro porous and high surface area magnesium carbonate

15 according to the invention may be provided as a mixture or composite with other materials, for example for the purpose of tailoring certain properties. As appreciated by the skilled person unavoidable impurities and intermediate products may be present in the final product. The remaining part of the material may be any amorphous or crystalline, organic or inorganic element or compound. Non limiting examples of such other material include salts, like

20 calcium carbonates, crystalline magnesium carbonates, sodium chloride, magnesium nitrate, copper sulfate, hydroxyapatite, strontium acetate, zinc citrate, hydroxides like magnesium hydroxide, strontium hydroxide and silicon hydroxide, oxides like magnesium oxide, iron oxide, silicon dioxide, aluminum oxide, aluminosilicate, metals like gold, silver, zinc, aluminum, as well as organic compounds like cellulose, spider silk and synthetic polymers.

According to one aspect of the present invention the magnesium carbonate of the present invention is produced and used as a functional material in dehumidification procedures. A non-limiting example of such dehumidification procedures includes sorption dehumidification to dehumidify the air in a so-called drum dehumidifier. In such processes, the humid air may enter through a rotor containing the magnesium carbonate of the present invention or a composite thereof that acts as a desiccant in the dehumidifier, and exits as a dry air. The magnesium carbonate of the present invention or a composite thereof can also be fixed on a porous matrix in the rotor in order to increase the airflow through the rotor; this porous matrix can for example be produced from paper. To regenerate the material, warm (e.g. temperatures between 70 and 300 °C) air is blown through a part of the rotor.

According to a further aspect of the invention the magnesium carbonate of the present invention or composites thereof is used as dehumidifying agent for organic solvents. The solvents may be selected from but are not limited to acetone, acetonitrile, benzol, chloroform, cyclohexane, diethylether, dichlormethane, diisopropylether, dimethylformamide, dioxane, ethylesther of acetic acid, methylesther of acetic acid, ethanol, n-hexane, methanol, isopropanol, pyridine, tetrahydrofurane, toluol, xylol.

According to a yet another aspect of the invention magnesium carbonate of the present invention or composites thereof is used as anti-caking agents to keep powders free flowing in production lines and in products under moist conditions. The magnesium carbonate of the present invention or composites thereof renders its action by dehumidification of the powder bed. Typical examples include, but are not limited to, production lines in food, pharmaceutical and polymer industries, as well as products such as table salt and flour.

According to a yet another aspect of the invention magnesium carbonate of the present invention or non-toxic composites thereof is used as a pharmaceutical additive to improve the powder flow during tableting.

According to a yet another aspect of the invention the magnesium carbonate of the present invention or non-toxic composites thereof is used as a porous pharmaceutical carrier for  
5 active pharmaceutical ingredients. The carrier is particularly useful to improve the apparent solubility of poorly soluble Type II and Type IV drugs according to BSC classification. The material of the present invention may also be used as a pharmaceutical additive which protects moisture-sensitive drugs from degrading.

10 A further aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof in pharmaceutical formulations as an excipient in order to protect moisture sensitive substances from contact with moisture. The magnesium carbonate will act as a moisture sink in the formulation and adsorb moisture present in the formulation.

15 One aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof as a material which is useful as a hand drying agent and a material improving the grip for sports and recreation, including weight lifting and climbing.

Yet another aspect of the present invention includes the production and use of the magnesium  
20 carbonate of the present invention or composites thereof as a material for drying packages, containers, cargo etc. during transportation and storage.

Another aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof as porous filler material in vacuum insulation panels used for thermal and/or acoustic insulation.

Another aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof in thermochemical energy storage device which utilizes the energy released due to water vapor adsorption. Such thermochemical energy storage is particularly useful in electric appliances including, but not limited to, dishwashers, refrigerators and climate control equipment.

In an additional aspect of the present invention the magnesium carbonate of the present invention or composites thereof are produced and used in agriculture applications. A non-limiting example of such applications includes the use of the magnesium carbonate of the present invention or composites thereof as a carrier of essential oils for pest control. The insect or bug repellent oils are stabilized and slowly released from the porous carriers in order to achieve a long-term repellent effect.

Another aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof to protect crops, and other types of food stuff, in bulk storages against insects, bugs and other unwanted organisms by utilizing the dehumidifying action of the magnesium carbonate of the present invention. The insects, bugs, pest and other unwanted organisms are selected from but not limited to beetles, flies, weevils, worms, moths, mold and cockroaches.

Yet another aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof to expelling insects, bug and other unwanted organisms from houses, buildings and storage rooms/containers by utilizing the dehumidifying action of the magnesium carbonate of the present invention.

A further aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof is in microbial and probiotic formulations preventing moisture to affect the active components in the formulations. By acting as a moisture sink, the magnesium carbonate can stabilize the formulation, minimize  
5 the amount of available moisture that can affect the active components, and hinder degradation of the same.

A further aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof as an oil, fat or sweat adsorbing agent in cosmetics and cosmeceuticals included but not limited to dry shampoos, face and  
10 body powders, formulations to treat or prevent acne, formulations for eczema prone skin. Herein and below the term cosmeceutical refers to the combination of cosmetics and pharmaceuticals. Cosmeceuticals are, thus, cosmetic products with biologically active ingredients purporting to have medical or drug-like benefits.

A further aspect of the present invention includes the production and use of the magnesium  
15 carbonate of the present invention or composites thereof for delivery of moisture, oil or fat to skin when the material is used in skin moisturizer products.

A further aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof as a cleansing agent that adsorbs impurities from the skin, as well as acts as an astringent and helps to close pores.

20 A further aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof for delivery of fragrances where the magnesium carbonate of the present invention or composites thereof acts as a carrier for the fragrances. Typical applications are selected from but not limited to cosmetics, perfumes,



skin-care products and products for odour control in domestic environments, cars, warehouses, industry buildings, waste disposal sites, sewage plants and public toilets.

A further aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof to improve the ability for cosmetic  
5 products to take up moisture.

Yet another aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof for air sanitation through uptake/adsorption of molecules causing undesired smells where the magnesium carbonate of the present invention or composites thereof acts as an adsorbent for the airborne molecules.  
10 The adsorbing material can be used in air filter systems or as stand-alone adsorbents. Typical applications are selected from but not limited to domestic odour control as well as odour control in cars, warehouses, industry buildings, waste disposal sites, sewage plants and public toilets. The amorphous and anhydrous magnesium carbonate renders its action through adsorbtion of vapors.

15 One additional aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof for air sanitation preventing or treating yeast damage of living spaces and commercial facilities by adsorbing geosmin and dehumidifying air to prevent yeast proliferation.

One additional aspect of the present invention includes the production and use of the  
20 magnesium carbonate of the present invention or composites thereof for air sanitation following fire damage.

One additional aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof as a fire retardant.

One additional aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof as a biomaterial in applications including but not limited to: bone void fillers, depot drug delivery systems and delivery vehicles for local release of therapeutic agents, as well as bone and cartilage repair materials.

One additional aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof for collection of toxic waste where the magnesium carbonate of the present invention or composites thereof is used as an adsorbent. In such applications, the material may be spread out over the toxic liquid, which subsequently is adsorbed into the material. After complete adsorption of the toxins, the material can be removed and discarded.

In an additional aspect of the present invention the magnesium carbonate of the present invention or composites thereof are produced and used for collection of oil spill. In such applications, the material may be spread out over the oil and the material adsorbs the oil. After complete adsorption of the oil, the material can be removed and the oil can be retrieved from the material elsewhere.

A further aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof in peeling or polishing applications. Non-limited examples of such applications include peeling creams, lotions, solutions and the like for face and body as well as tooth pastes and other dental formulations with polishing properties. In such applications the magnesium carbonate of the present invention may optionally be loaded with a functional agent improving the action of the peeling or polishing application. Non-limiting examples of such agents include flour, whitening agents, vitamins, retinoic acid, trichloroacetic acid, phenol, alpha hydroxy acids like, e.g., glycolic acid, fruit

acids like, e.g., citric acid, glycolic acid, lactic acid, malic acid and tartaric acid, beta hydroxy acids like, e.g., salicylic acid.

A further aspect of the present invention includes the production and use of the magnesium carbonate of the present invention or composites thereof is the use of the magnesium  
5 carbonate to alter the viscosity and consistency of ink.

## BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described in detail with reference to the drawing figures, wherein:

- Figure 1. is a graph illustrating the XRD diffraction pattern for a magnesium carbonate of the present invention, wherein the halo at  $2\Theta \sim 30^\circ$  indicates the presence of at least one amorphous phase and the sharp peaks belong to crystalline MgO;
- Figure 2. is a graph illustrating the Raman spectrum for a magnesium carbonate of the present invention, wherein the peak at  $\sim 1100 \text{ cm}^{-1}$  is from the carbonate group and the broad halo with centrum at  $100 \text{ cm}^{-1}$  is a Boson peak;
- Figure 3. is a graph illustrating the TGA and dTGA/DTA curves for a magnesium carbonate of the present invention, illustrating how the decomposition at  $390^\circ\text{C}$  pertains to  $\text{MgCO}_3$  and the decomposition prior to that (i.e. observed at lower temperatures) is due to the loss of remaining organic groups;
- Figure 4. is a graph illustrating the dTGA curves for a magnesium carbonate of the present invention, wherein the sample has been stored at 100% humidity and room temperature for the displayed time periods and no visible change in the peak position for the peak at approximately  $440^\circ\text{C}$  can be seen;
- Figure 5. is a graph illustrating the water sorption isotherms at room temperature for a magnesium carbonate of the present invention (named Upsalite in the figure),  $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , Aerosil and Zeolit Y.;
- Figure 6. is a graph illustrating the nitrogen sorption isotherm for a magnesium carbonate of the present invention;
- Figure 7. is a graph illustrating the nitrogen sorption isotherm for hydromagnesite  $(\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O})$ ;

Figure 8. is a graph illustrating the DFT-based pore size distribution for a magnesium carbonate of the present invention, wherein the pore size distribution has a maximum around 3 nm and the cumulative pore size distribution gives that 98% of the pore volume is constituted of pores with a diameter smaller than 6 nm;

5 Figure 9. is a graph illustrating the XPS O<sub>1s</sub> peak for a magnesium carbonate of the present invention, wherein the peak at 533.5 eV belongs to MgCO<sub>3</sub> (solid squares in curve fit), the peak at 531.0 eV belongs to MgO (solid circles in curve fit) and the peak at 535.6 eV belongs to surface adsorbed water (open triangles in curve fit). (the solid lines represent the recorded spectrum; open squares represent the subtracted  
10 background;

Figure 10. is a graph illustrating the FTIR spectrum for a magnesium carbonate of the present invention, wherein the three visible bands (1440 cm<sup>-1</sup>, 1100 cm<sup>-1</sup> and 650 cm<sup>-1</sup>) are all due vibrations of the carbonate group;

Figure 11. is a graph illustrating the XPS Mg<sub>2p</sub> peak for a magnesium carbonate of the  
15 present invention, wherein the peak at 52.1 eV belongs to MgCO<sub>3</sub> (solid circles in curve fit) and the solid line represents the recorded spectrum and the open squares represent the subtracted background;

Figure 12. is a SEM image of a magnesium carbonate of the present invention;

Figure 13. is a graph illustrating the nitrogen sorption isotherm of a magnesium carbonate of  
20 the present invention in which the synthesized powder was heat-treated at 70°C for 7 days (example 2);

Figure 14. is a graph illustrating the DFT-based pore size distribution for a magnesium carbonate of the present invention in which the synthesized powder was heat-treated at 70°C for 7 days (example 2);

25 Figure 15. Is a SEM image of a spray-dried magnesium carbonate of the present invention;

Figure 16. is a graph illustrating the water sorption isotherm at room temperature for a spray-dried magnesium carbonate of the present invention;

Figure 17. is a graph illustrating the DFT-based pore size distribution of spray-dried magnesium carbonate of the present invention;

5 Figure 18. is a graph illustrating the Nitrogen sorption isotherm for a spray-dried a magnesium carbonate of the present invention;

Figure 19. is a graph illustrating the DFT-based pore size distribution for a magnesium carbonate of the present invention (example 4);

Figure 20. is a graph illustrating the weight increase for the magnesium carbonate according  
10 to example 3 when stored in a sealed vessel saturated with water vapor at different time periods, at room temperature;

Figure 21. is a graph illustrating the DFT-based pore size distribution for the magnesium carbonate of the present invention as prepared in example 5;

Figure 22. is a graph illustrating the DFT-based pore size distribution for the magnesium  
15 carbonate of the present invention as prepared in example 6;

Figure 23. is a graph illustrating the DFT-based pore size distribution for the magnesium carbonate of the present invention as prepared in example 7;

Figure 24. is a graph illustrating the DFT-based pore size distribution for the magnesium carbonate of the present invention as prepared in example 8;

20 Figure 25. is a graph illustrating the DFT-based pore size distribution for the magnesium carbonate of the present invention as prepared in example 10;

Figure 26. is a graph illustrating the nitrogen sorption of the magnesium carbonate material as prepared in example 15;

Figure 27. is a graph illustrating the DFT-based pore size distribution for the magnesium  
25 carbonate material as prepared in example 15;

Figure 28. is a graph illustrating the moisture adsorption of the magnesium carbonate material as prepared in example 15;

Figure 29. Illustrates the X-ray diffraction pattern for the material as prepared in example 24, wherein the peaks correspond to crystalline nesquehonite;

5 Figure 30. is a graph illustrating the EGA data for a representative sample of the magnesium carbonate according to the invention;

Figure 31. is a graph illustrating the growth in pore size associated with decomposition of organic groups and evolution of  $H_2O$ ,  $CO_2$  and  $H_2$  from the magnesium carbonate according to the invention;

10 Figure 32. is a graph illustrating the IR spectrum for the material as prepared in example 26;

Figure 33. is a graph illustrating the regeneration temperature needed to remove adsorbed water from the magnesium carbonate as prepared in example 27 as compared to Zeolite;

Figure 34. is a graph illustrating the pore size distribution (incremental pore volume in a.u.)  
15 obtained from the  $N_2$  sorption analysis of isotherms recorded on the calcined magnesium carbonate material as prepared in example 28 (curve with open circles) as well as on the ibuprofen loaded  $MgCO_3$ -IBU sample (curve with solid triangles) of the same example;

Figure 35. is a graph illustrating the dissolution profile of free ibuprofen (dashed lower  
20 curve) and ibuprofen incorporated in the magnesium carbonate as prepared in example 28 (solid upper curve) recorded at pH 6.8;

Figure 36. is a graph illustrating the water sorption isotherms at room temperature for a calcined magnesium carbonate of the present invention as prepared in example 29.

25

## DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a novel anhydrous, amorphous, micro porous, high  
5 specific surface area magnesium carbonate with extraordinary moisture sorption properties.  
As is described in detail herein, the material is suitable for use in a wide variety of  
applications.

The novel anhydrous, amorphous, micro porous, high specific surface area (between 60 and  
1500 m<sup>2</sup>/g) magnesium carbonate according to the invention may be provided as a mixture or  
10 composite with other materials, for example for the purpose of tailoring certain properties. As  
appreciated by the skilled person unavoidable impurities and intermediate products may be  
present in the final product. The remaining part of the material may be any amorphous or  
crystalline, organic or inorganic element or compound. Non limiting examples of such other  
material include salts, like calcium carbonates, crystalline magnesium carbonates, sodium  
15 chloride, magnesium nitrate, copper sulfate, hydroxyapatite, strontium acetate, zink citrate,  
hydroxides like magnesium hydroxide, strontium hydroxide and silicon hydroxide, oxides  
like magnesium oxide, iron oxide, silicon dioxide, aluminum oxide, aluminosilicate, metals  
like gold, silver, zink, aluminum, as well as organic compounds like cellulose, spider silk and  
synthetic polymers.

20 Different suitable methods may be employed, individually or combined, to confirm and  
quantify the amorphous magnesium carbonate content of the material. These methods can  
include, but are not limited to, XPS (x-ray photoelectron spectroscopy), Raman spectroscopy,  
XRD (x-ray diffraction), FTIR (Fourier transform infrared spectroscopy), NMR spectroscopy  
(nuclear magnetic resonance spectroscopy), ICP-MS (inductively coupled plasma mass  
25 spectrometry), EDS (energy-dispersive X-ray spectroscopy), TEM (transmission electron



microscopy) ED (electron diffraction) and TGA (Thermogravimetric analysis). As described in Example 1 below, Raman spectroscopy may be employed to reveal the presence of amorphous magnesium carbonate in the material (by the presence of the so called Boson peak at low wavenumbers which is characteristic for amorphous materials, and the distinctive carbonate peak at  $\sim 1100\text{ cm}^{-1}$ ). To confirm the presence and determine the amount of magnesium carbonate in a material, XPS analysis can be employed in the following manner: The magnesium carbonate content in the material can be determined by elemental analysis using XPS, and energy resolved spectrum analysis using the same technique can be used to distinguish between crystalline and amorphous magnesium carbonate: the electron binding energy in the Mg 2s orbital of amorphous magnesium carbonate is expected to be  $\sim 90.7\text{ eV}$  while the binding energy generally is expected to be  $\sim 91.5\text{ eV}$  or higher for crystalline magnesium carbonates. The presence of structural water, i.e. hydrated magnesium carbonates, can be elucidated via energy resolved XPS analysis of the O1s peak as described in one of the embodiments below. Other techniques can involve XRD analysis for crystal phase determination of the constituents of a material where the amorphous magnesium carbonate content can be quantified in relation to the crystalline content.

In particular, the presence of amorphous magnesium carbonate can be confirmed by XRD. In an XRD measurement amorphous magnesium carbonate gives rise to either broad halos or just noisy flat signals in the  $2\theta$  window between about  $10^\circ$  and  $20^\circ$  as well as between about  $25^\circ$  and  $40^\circ$  when the diffractometer uses  $\text{CuK}\alpha$  radiation. Example of such halos can be seen in Fig. 1. When the remaining part of a material, consisting of materials other than amorphous magnesium carbonate (including impurities or other elements introduced on purpose), such materials will give rise to peaks in the XRD pattern, as also exemplified in Example 1, and seen in Fig. 1, provided that they are crystalline.

The amorphous magnesium carbonate according to the present invention is anhydrous. Anhydrous in this respect means that no structural water is associated with the bulk of the material, however water molecules are allowed to be tightly or loosely bound to the surface of the material. In this context, tightly bound water does not imply non-regenerable water  
5 (details concerning regenerating moisture sorption ability the amorphous magnesium carbonate of the present invention are described below). Absence of structural water can be verified using X-ray photoelectron spectroscopy (XPS) following sputter cleaning of the surface under vacuum as exemplified in Fig 9. The lack of structural water in the bulk is verified by energy resolved analysis of the O1s peak: a properly calibrated O1s spectra should  
10 contain a peak at  $\sim 533.5$  eV corresponding to  $\text{MgCO}_3$ , however no peak component corresponding to  $\text{H}_2\text{O}$  or OH-groups should be present in the spectrum other than that for surface adsorbed water which is expected around 535.6 eV.

The magnesium carbonate according to the present invention has a cumulative pore volume of pores with a diameter smaller than 10 nm of at least  $0.018 \text{ cm}^3/\text{g}$ , preferably above  $0.4 \text{ cm}^3/\text{g}$ ,  
15 preferably above  $0.6 \text{ cm}^3/\text{g}$  or even more preferably above  $0.8 \text{ cm}^3/\text{g}$ , and a cumulative pore volume of pores with a diameter smaller than 10 nm up to  $1.5 \text{ cm}^3/\text{g}$ , or more preferably up to  $2 \text{ cm}^3/\text{g}$  or most preferably up to  $3 \text{ cm}^3/\text{g}$  which is illustrated in Figs. 8, 14, 17, 19, 21, 22, 23, 24 and 25.

The pore size distribution and the cumulative pore volume specified in the above  
20 embodiments may be determined by density functional theory (DFT) calculations on the adsorption isotherm with appropriate assumptions about pore shape as exemplified in Figs. 8, 14, 17, 19, 21, 22, 23, 24 and 25.

The combination of amorphicity and presence of micro pores in the amorphous magnesium carbonate of the present invention, as specified in the above embodiments, is considered to be

important for the moisture sorption properties of the material. As is obvious from Figures 5 and 16 the amorphous magnesium carbonate of the present invention has a dramatically higher moisture sorption ability at low and intermediate RH as compared to for example the pharmaceutical grade of magnesium carbonate (crystalline hydromagnesite, see Fig. 5) and an amorphous magnesium carbonate that has a volume of pores with a diameter smaller than 10 nm below  $0.018 \text{ cm}^3/\text{g}$ , see Fig. 28.

The amorphous magnesium carbonate according to the present invention, features a specific surface area of at least  $60 \text{ m}^2/\text{g}$ , preferably of at least  $100 \text{ m}^2/\text{g}$ , more preferably of at least  $240 \text{ m}^2/\text{g}$ , even more preferably of at least  $350 \text{ m}^2/\text{g}$ , most preferably of at least  $600 \text{ m}^2/\text{g}$ , and a SSA up to  $400 \text{ m}^2/\text{g}$ , preferably up to  $800 \text{ m}^2/\text{g}$ , more preferably up to  $1000 \text{ m}^2/\text{g}$ , even more preferably up to  $1200 \text{ m}^2/\text{g}$  and most preferably up to  $1500 \text{ m}^2/\text{g}$ .

The specific surface area can be determined by employing the BET method to nitrogen adsorption isotherms like those presented in Figs. 6 and 13. More precisely a multipoint BET analysis is performed on the relative pressure range between 0.05 and 0.3 of the adsorption branch of a nitrogen isotherm performed at boiling nitrogen temperature. If the BET equation does not yield a linear slope in this pressure range, the BET analysis should be employed on a more narrow pressure range for accurate result. The nitrogen adsorption analysis can be performed on an ASAP 2020 from Micromeritics after drying the sample at  $70^\circ\text{C}$  for 2 days. Prior to analysis, the sample tube containing the sample is evacuated with a vacuum set point at  $10 \mu\text{m Hg}$  and heated to at  $95^\circ\text{C}$  for 10h with a ramping rate of  $1^\circ\text{C}/\text{min}$ . It should be noted that in the cases when the specific surface area of the amorphous magnesium carbonate of the present invention are of the order of  $500 \text{ m}^2/\text{g}$  or larger it is comparable to that of the exclusive class of high surface area materials such as zeolites, mesoporous silicas, metal organic framework materials, and carbon nanotubes.

A large surface area, i.e. larger than the surface area of a macroscopic solid material, is beneficial for all industrial applications where surface interactions are of importance, including but not limited to drug delivery, catalysis, adsorption of various gases and liquids. It can be appreciated by one skilled in the art that being able to produce an amorphous magnesium carbonate according to the present invention of high surface area will improve the functionality of the material in a range of applications like those mentioned in the summary of invention.

To one skilled in the art it is obvious that the surface area of any material can be increased by diminishing the particle size of said material. A diminished particle size may also increase the amorphicity of a material as measured by XRD. Large surface areas and amorphicity stemming only from such diminishing of the particle size is generally not expected to lead to improved properties in applications of magnesium carbonates in the applications mentioned above and in the examples as well as in other application.

With reference to the above; in one specific embodiment of the present invention the amorphous magnesium carbonate of the present invention with the surface areas detailed above, consists of particles having an equivalent to a sphere diameter of not smaller than 37 nm for more than 1% of their number size distribution.

Another way of assessing the presence of micro pores in the material of the present invention and also assessing a large surface area is by a direct study of nitrogen sorption isotherms.

Thus, according to one embodiment of the present invention the amorphous magnesium carbonate of the invention adsorbs more than 20 cm<sup>3</sup> nitrogen/g material at STP at a partial nitrogen pressure of 0.5, preferably more than 25 cm<sup>3</sup> nitrogen/g material at STP, even more preferably more than 30 cm<sup>3</sup> nitrogen/g material at STP, even more preferably more than 50 cm<sup>3</sup> nitrogen/g material at STP, even more preferably more than 100 cm<sup>3</sup> nitrogen/g material

at STP, even more preferably more than 200 cm<sup>3</sup> nitrogen/g material at STP, even more preferably more than 250 cm<sup>3</sup> nitrogen/g material at STP during a nitrogen adsorption analysis. The nitrogen adsorption ability is confirmed from gas adsorption experiments like those exemplified in Figs. 6 and 13.

- 5 The amorphous magnesium carbonate according to the present invention is stable upon storage for up to 13 weeks or longer. Experiments have shown that the materials can be stable up to 3-5 months and even longer at room temperature and relative humidities above 20%. In some experiments the stability for several months was verified when the material was stored at 30%, 50, 60%, and also in a sealed humidity cabinet with a saturated water vapor
- 10 atmosphere. The stability of the magnesium carbonate component can be assessed by Differential Thermogravimetric measurements (also commonly denoted as DTA or dTGA measurements in the literature) as exemplified in Fig. 3 and Fig. 4 by observing the peak related to the decomposition of the carbonate at above 350 °C. More precisely the analysis is performed with a Thermogravimetric analyzer from Mettler Toledo, model TGA/SDTA851e.
- 15 Approximately 15 mg of sample is placed in an inert aluminum cup and heated from room temperature to 700 °C under a flow of air where the temperature ramping rate is 10 °C/min during analysis. The stability of the material is confirmed by the lack of changes in this peak upon storage in a moisture containing atmosphere and also by the fact that the position of the peak is not shifted noticeably (i.e. more than 10-20 °C) towards lower temperatures. A peak
- 20 shift towards higher temperatures is however, to be taken as an evidence for stability. Such shifts towards higher temperatures can for example be observed when comparing the experiments performed on a dry amorphous magnesium carbonate according to the present invention, Fig. 3, with those performed on amorphous magnesium carbonate according to the present invention stored for different time periods at saturated water vapor, Fig. 4. For an
- 25 unstable material, on the other hand, the carbonate decomposition peak at above 350 °C is

expected to develop a shoulder and/or split into two or more peaks and also to move towards lower temperatures as is the case e.g. for the magnesium carbonate material described in Botha et al. 2003. The stability of the material of the present invention is industrially favorable when it comes to use in e.g. moist environments and ensures that the material can be transported, stored and also used at high relative humidity at prolonged time periods without, due to structural changes, losing its functional abilities as disclosed in the present invention.

The amorphous magnesium carbonate according to the present invention adsorbs more than 0.3 mmol water /g material at an RH of 1% at 25°C. In some experiments it adsorbs more than 0.8 and even more than 1.5 mmol water/g material. As exemplified in Fig. 5, certain experiments have shown that the material adsorbs even more than 2.4 mmol water /g material at this low relative humidity. The water vapor adsorption ability can be confirmed by first drying the material at 70°C during at least 48 hours and then performing a water vapor sorption experiment as that exemplified in Fig. 5 and Fig. 16. More specifically this can be performed with an ASAP 2020 from Micromeritics equipped with a water vapor source. Prior to analysis, the sample tube containing the sample is evacuated with a vacuum set point at 10µm Hg and heated to 95°C for 10h with a ramping rate of 1°C/min. The measurement is performed at 25°C starting at low RH with increasing amounts of water vapor dosed into the sample tube. The amount of moisture adsorbed on the material at a given relative humidity is measured when equilibrium between adsorbed and free water vapor is reached in the sample tube. Equilibrium in this case is defined as follows: equilibrium is reached when the pressure change per equilibrium interval (first derivative) is less than 0.01% of the average pressure during the interval. The time interval is set to 50 sec during the measurement. In one particular aspect of the embodiment the moisture sorption properties of the amorphous magnesium carbonate of the present invention is comparable, or even superior, to those of

hydrophilic zeolites, e.g. zeolite Y (600 m<sup>2</sup>/g, silica/alumina ratio 5.2:1) and also superior to those of commonly used desiccants, e.g. fumed silica (Aerosil) or crystalline hydromagnesite. An example of such a material according to the present invention is given in Fig. 5.

5 The amorphous magnesium carbonate according to the present invention adsorbs more than 0.5 mmol water/g material at an RH of 2% at 25°C. Experiments have shown that the material adsorbs more than 0.8 or even more than 2.0 mmol water/g material, while other experiments have shown that it adsorbs even more than 3.5 mmol water/g material (see e.g. Fig. 5). The water vapor sorption ability was confirmed as described above.

10 The amorphous magnesium carbonate according to the present invention adsorbs more than 0.6 mmol water /g material at an RH of 5% at 25°C, and even more than 5.3 mmol water/g material. The water vapor sorption ability was confirmed as described above.

The amorphous magnesium carbonate according to the present invention adsorbs more than 1.0 mmol water /g material at an RH of 10% at 25°C and even more than 6.3 mmol water/g material. The water vapor sorption ability was confirmed as described above.

15 The amorphous magnesium carbonate according to the present invention adsorbs more than 1.0 mmol water/g material at an RH of 20% at 25°C and even more than 8.3 mmol water/g material. The water vapor sorption ability was confirmed as described above.

20 The amorphous magnesium carbonate according to the present invention adsorbs more than 1.5 mmol water/g material at an RH of 50% at 25°C and even more than 10.3 mmol water/g material. The water vapor sorption ability was confirmed as described above.

The amorphous magnesium carbonate according to the present invention adsorbs more than 5.0 mmol water /g material at an RH of 90% at 25°C and even more than 13.5 mmol water /g material. The water vapor sorption ability was confirmed as described above.

The amorphous magnesium carbonate according to the present invention retains more than 30 wt% of adsorbed moisture when the RH is lowered from 90% to 5% during a water vapor desorption analysis performed at 25°C as exemplified in Fig. 5 and 16. Typically the material retains more than 50 wt% or 60 wt% of the adsorbed moisture and even more than 80 wt% of the adsorbed moisture. More precisely the analysis is performed immediately after a water vapor adsorption analysis as described above by lowering the water vapor pressure in the sample tube. The desorption analysis is allowed to start once the RH has reached and equilibrated at at least 94% RH in the sample tube. During the desorption study, the RH in the sample tube is lowered stepwise and the amount of desorbed vapor is measured at specified relative humidities. The amount of water vapor desorbed from the material at a given relative humidity is measured when equilibrium between adsorbed and free water vapor is reached in the sample tube. Equilibrium in this case is defined as follows: equilibrium is reached when the pressure change per equilibrium interval (first derivative) is less than 0.01% of the average pressure during the interval. The time interval is set to 50 sec during the measurement.

The amorphous magnesium carbonate according to the present invention retains more than 40 wt% of adsorbed moisture when the RH is lowered from 90 % to 20% during a water vapor desorption analysis performed at 25°C as exemplified in Fig. 5 and Fig. 16. The water vapor retention ability was confirmed as described above.

The ability to retain moisture in the structure upon lowering of the relative humidity after moisture sorption as described in the above embodiments is a highly favorable property of the material according to the present invention and rather unique amongst moisture adsorbents as exemplified in Fig. 5. As will be appreciated by one skilled in the art, the fact that the material of the present invention not easily lets go of the moisture adsorbed when a lowering of humidity is performed after adsorption prevents moisture from being released to the



environment from which it was removed by an accidental or purposeful lowering of the surrounding humidity. As will become clear from below, the fact that only minor energy input is needed to release the moisture adsorbed in the structure to regenerate the moisture sorption properties of the material is an additionally beneficial property of the material of the present invention since it e.g. opens up for energy efficient regeneration of moisture sorption materials.

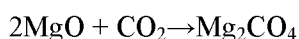
The moisture sorption properties of the amorphous magnesium carbonate of the present invention can be regenerated after storing the material at RH higher than 90% RH for at least 7 days at room temperature. This can be performed by drying the material at elevated temperatures at 250°C or more preferably at 150 °C, even more preferably at 110 °C, or even more preferably at 95 °C or below. A person skilled in the art will be able to determine the time needed to dry the material sufficiently and will find that a longer drying time is needed for low drying temperatures. Applying vacuum to the material during the drying procedure will obviously decrease the time needed for removal of adsorbed water species from the material. When drying, for example, 0.2 g of material at 95°C under vacuum with a vacuum set point of 10 µm Hg the drying time is typically 5 days or shorter. Experiments have shown that the drying time can be 2 days and even only 20 h or less.

The fact that the moisture sorption properties of the material of the present invention may be regenerated can be confirmed by the fact that at least one of the moisture sorption properties described above is still valid (adsorption properties below 1%, 2%, 5% 10, 20 and 50% RH and/or adsorption properties below 90% RH and/or desorption properties from 90% RH to 5% RH and/or desorption properties from 90% RH to 20% RH).

*Theoretical discussion about the reaction mechanism*

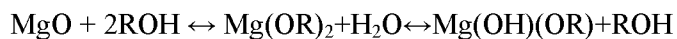
The amorphous and micro porous magnesium carbonate according to the present invention,  $\text{Mg}_x\text{CO}_y$ , wherein  $x=1-2$  and  $y=3-4$ , is obtained upon drying of a reaction product between  $\text{MgO}$  and  $\text{CO}_2$  (mildly pressurized) in methanol. The  $\text{Mg}_x\text{CO}_y$  material disclosed here is  
5 amorphous, and, because it is currently not possible to distinguish between several amorphous compositions of  $\text{Mg}_x\text{CO}_y$ , it includes  $\text{MgCO}_3$ ,  $\text{MgCO}_3 \cdot \text{MgO}$ , and  $\text{Mg}_2\text{CO}_4$ , although preferably  $x=1$  and  $y=3$ , and any of their combinations as well as their solvates.

For the sake of simplicity, the basic reaction of magnesium carbonate formation from  $\text{MgO}$  and  $\text{CO}_2$  in alcohol could be condensed into the following terms:



However, the reaction between solid  $\text{MgO}$  and gaseous  $\text{CO}_2$  does not readily proceed or is too slow, and one skilled in the art will understand that in reality the reaction scheme is much more complex and involves several important intermediates which form in the alcohol phase.  
15 By considering the role of these important intermediates, which will be highlighted below, one skilled in the art will also appreciate that the final product, i.e.  $\text{Mg}_x\text{CO}_y$ , could be obtained in many ways, i.e. without direct use of  $\text{MgO}$ , including metallic  $\text{Mg}$  or several  $\text{Mg}$  containing inorganic and organic compounds. Therefore, the reaction scheme proposed herein below should not be perceived in limiting terms.

20 In the old literature, it has often been considered that oxides of alkali and alkaline earth metals in alcohols form oxides with alcohol of crystallization, i.e.  $\text{MeO} \cdot n\text{ROH}$ . The modern understanding though suggests that, when dissolved in alcohol,  $\text{MgO}$  forms alcoholates (also called alc oxides).



*The double-sided arrow above and all other throughout the text should be interpreted as  $\rightleftharpoons$ , i.e. referring to a reversible reaction.*

ROH represents an alcohol which can be any kind of alcohol including aliphatic, alkenyl,  
 5 aromatic, primary, secondary, tertiary alcohol as well as glycol or polyol. Both Mg alcoholate and Mg hydroxyalcoholate could be formed during the course of the reaction. The fact that the reaction proceeds in the indicated order was confirmed by following the isotopic exchange in the  $\text{CaO-C}_2\text{H}_5\text{OH-H}_2\text{O}$  system. It has further been discussed in the literature that tertiary systems of alkaline earth metal oxides in alcohol+water can show complex phase diagrams of  
 10 varying compositions which include not only the  $\text{Me(OR)}_2$  or  $\text{Me(OH)(OR)} \cdot n\text{ROH}$ , as expected from the reaction above, but also  $\text{Me(OH)}_2 \cdot n\text{ROH}$ . Thus, one skilled in the art will appreciate that  $\text{Mg}_x\text{CO}_y$  disclosed herein could also be obtained from any of the above intermediates by considering the appropriate proportions between the components of the tertiary mixtures as well as availability of water in the system and in situ hydrolysis of then-  
 15 present compounds and their solvates. FTIR analysis of the samples studied did not reveal the presence of  $\text{Mg(OH)}_2 \cdot n\text{ROH}$  in the system.

During the development of the magnesium carbonate disclosed herein it was found that heating the solution of MgO in alcohol, e.g. 50°C, prior to or during the pressurization with  $\text{CO}_2$  was beneficial for high yield of  $\text{MgOHOCH}_3$ , that currently are considered to be an  
 20 intermediate in the reaction.

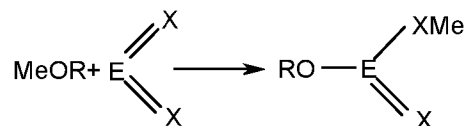
Considering that Mg alcoholates could be important intermediates, one skilled in the art will further assert that Mg alcoholates could also be obtained using other chemical routes which could include but are not limited to:

- Reaction of metallic Mg with alcohol;

- Reaction of  $\text{Mg}(\text{OH})_2$  with alcohol;
  - Reaction of Mg amines with alcohol in liquid  $\text{NH}_3$  as solvent;
  - Decomposition of Mg hydride, carbide, nitride, amide, sulfide or organometallic compounds containing Mg;
- 5
- Metatheses of Mg salts with alcoxide of other metals;
  - Metatheses of alcoxides with alcohols leading to a synthesis of new alcoxides;
  - Oxidation of alkyl derivatives with oxygen;
  - Reduction of carbonyl-containing compounds;
  - Electrochemical reactions in alcohols, e.g. using metallic Mg as the anode or
- 10
- electrolysis of Mg salts.

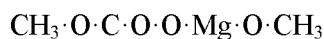
Alcoxides of metals are very sensitive to moisture, air, and carbon dioxide and behave as “strong base”. They can therefore interact both with acids and their anhydrides.

The typical reaction of an alcoxide with acid follows as:



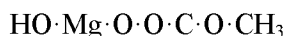
- 15
- Wherein  $\text{E}=\text{C}$  or  $\text{S}$ , and  $\text{X}=\text{O}$  or  $\text{S}$ ; and  $\text{Me}=\text{Li}$ ,  $\text{K}$ ,  $\text{Na}$ ,  $\text{Cs}$ ,  $\text{Rb}$ ,  $\text{Mg}$ ,  $\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$ ,  $\text{Tl}$ .

Upon interaction with  $\text{CO}_2$ , Mg methylate can form Mg dimethylcarbonate..



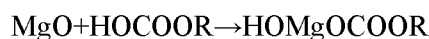
Mg dimethylcarbonate is similar to Mg hydrocarbonate except that the hydroxyl group is substituted by a metoxy group and thus behaves similarly with respect to acids and water.

- 20
- It should also be mentioned that monomethyl hydroxycarbonate salt of Mg have not been described,



which would otherwise be expected to exist considering the structure of Mg dimethylcarbonate. Monomethyl hydroxycarbonate of Mg is deemed an important intermediate for producing micro- and/or mesoporous  $\text{Mg}_x\text{CO}_y$  disclosed herein.

- 5 Another potentially important intermediate is hemicarbonic acid  $\text{HOCOOR}$ . The importance of the formation of hemicarbonic acid is highlighted by considering the possibility of the following reaction:



- During the development of our material it became clear that pressurizing  $\text{CO}_2$  gas (1-12  
10 bar) in the reaction vessel containing MgO in alcohol is important, which potentially enables the following reaction:



- The formation of hemicarbonic acid in  $\text{CO}_2$ -alcohol systems has been shown in supercritical fluids at 70-100 bar at 20-40°C for 2 days by interacting it with  
15 diazodiphenylmethane as a probe to catch acid species. These results also showed that in a homologous row of alcohols the rate of hemicarbonic acid formation is the fastest for methanol and the slowest for tert-butanol.

One skilled in the art will also understand that hemicarbonic acid can be produced by interacting monomethylcarbonate with an acid in an organic solvent, e.g. dimethyl ether,

- 20 
$$\text{MeOCOCH}_3 + \text{HCl} \rightarrow \text{HOCOCH}_3 + \text{MeCl}$$

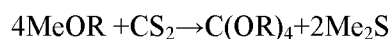
Thereby, it is also expected that for bivalent Me (e.g. Mg, Ca, Sr, Ba) dimethylcarbonates interacting with water- formed in situ or added in stoichiometric quantities- monomethyl

hydroxycarbonic salt and hemicarbonic acid could be obtained although no literature reports on this reaction exist so far.



Alkylesters of hemicarbonic acid are therefore deemed important intermediates for the formation of  $\text{Mg}_x\text{CO}_y$  disclosed herein.

Orthocarbonic acid,  $\text{H}_4\text{CO}_4$ , is another possible important intermediate which has never been isolated either in the form of free acid or its salts but only so far is known to exist in the form of esters, i.e.  $\text{C(OR)}_4$ , or substituted complex ester-salts, e.g.  $\text{NaCOF}_3$ . However, numerous computational models show that salts of orthocarbonic acid can exist. It should be noted that esters of orthocarbonic acid  $\text{C(OR)}_4$  can be produced from alcoxides of Sn, Tl, or Cu. In particular, for monovalent metals Tl, Cu the reaction scheme between alcoxides and carbondisulfide is the following:



Considering the similarity between  $\text{CS}_2$  and  $\text{CO}_2$  as acid anhydrides with substituted carbon chalcogenides, the reaction mechanism involving orthocarbonic acid esters  $\text{C(OR)}_4$  and its salts, i.e.  $\text{COMe}_4$  (for monovalent metals) and  $\text{COMe}_2$  (for bivalent metals), is therefore plausible yet it has never been proved. It is also expected that if  $\text{CO}_2$  were used instead of  $\text{CS}_2$  the final product should contain some metal oxide in analogy with metal sulfide formed as discussed above.

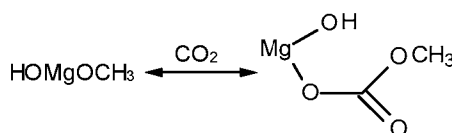
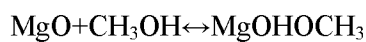
In all, it infers from above considerations that the mildly pressurized mixture of  $\text{MgO}$ ,  $\text{CO}_2$ , and alcohol represents a rather complex cocktail of different intermediates at equilibrium which can be shifted by changing the concentration, pressure, and

temperature of the system. By using FTIR-spectroscopy, the following two intermediates were clearly detectable, viz.  $\text{MgOHCH}_3$  and  $\text{HOMgOCOOCH}_3$ .

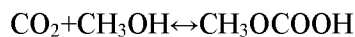
Therefore, the following chain of reactions, considering the case of methanol, is deemed beneficial for formation of  $\text{Mg}_x\text{CO}_y$  material disclosed herein:

5

Route 1 (monomethyl hydroxycarbonate route):



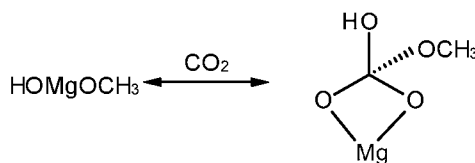
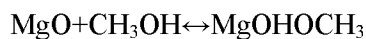
Route 2 (hemicarbonic acid route):



10



Route 3 (orthocarbonate route):



The routes 1, 2, and 3 are non-exclusive and may well occur in parallel under mild  $\text{CO}_2$  pressure (1-12 bar) and  $T=20-70^\circ\text{C}$ . One skilled in the art will also understand that if the reaction involving these intermediates is conducted in another solvent than alcohol the

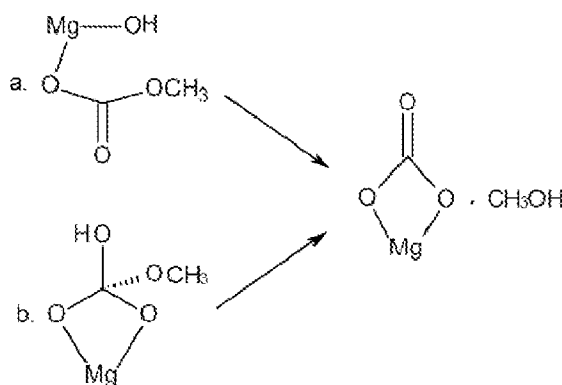
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suitable temperature range will depend on the boiling and freezing of the said solvent. It is noteworthy that the final product of reactions according to routes 1, 2, and 3, viz.

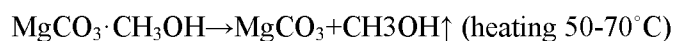
$\text{HOMgOCOOCH}_3$ , is a labile substance due to the hydroxyl group present in the vicinity of methoxide group and therefore could produce a solvate of  $\text{Mg}_x\text{CO}_y$  with alcohol of

5 crystallization, i.e.  $\text{Mg}_x\text{CO}_y \cdot \text{CH}_3\text{OH}$ . Upon mild heating  $\text{Mg}_x\text{CO}_y \cdot \text{CH}_3\text{OH}$  readily releases its alcohol of crystallization and produces a micro- and/or mesoporous powder of  $\text{Mg}_x\text{CO}_y$  as disclosed herein. Some possible reactions involving alcohol of crystallization are shown below:

Final:



10



That the product of  $\text{Mg}_x\text{CO}_y \cdot \text{CH}_3\text{OH}$  drying, e.g. at  $70^\circ\text{C}$ , is  $\text{Mg}_x\text{CO}_y$  was verified using FTIR spectroscopy. Obviously, the material can also be heated at higher temperatures as long as it does not decompose but this will be related to unnecessary energy consumption in industrial settings.

15

Upon visual observation, the degradation goes through several steps since first a gel like consistency is seen which then turns into a white rock, identified as amorphous,



anhydrous  $\text{Mg}_x\text{CO}_y$ . The mol distribution of the constituent elements, i.e. Mg, C, and O, in the final product suggested that the material can contain any of the following species  $\text{MgCO}_3$ ,  $\text{MgCO}_3 \cdot \text{MgO}$ , and/or  $\text{Mg}_2\text{CO}_4$ , which at this point could not be discerned due to the amorphous nature of the product.

5 Surprisingly, it was observed that the vapors/gases formed during the drying of the liquid phase cannot escape readily through the viscous gel phase and therefore act as templates around which the solidification occurs. These bubbles form the micro and/or mesopores in the produced  $\text{Mg}_x\text{CO}_y$  material and also stand for the extraordinarily high pore volume and surface area of the material disclosed herein. That the gases are trapped in the gel was  
10 further exemplified when vacuum (200 mbar) was employed to accelerate the drying at 70 °C: the semisolid phase behaved then as if it was boiling.

Brief synopsis of the mechanism, method, and possible important intermediates includes the following:

- Routes 1 (monomethyl hydroxycarbonate route), 2 (hemicarbonic acid route), and 3  
15 (orthocarbonate route) have not been previously shown to lead to formation of  $\text{MgOHOCOCH}_3$ ;
- $\text{MgOHOCOOCH}_3$  could be a labile but important intermediate which could readily produces a solvate of  $\text{Mg}_x\text{CO}_y \cdot \text{CH}_3\text{OH}$ ;
- $\text{MgOHCH}_3$  and  $\text{HOCOOCH}_3$  could be other important intermediates for producing  
20  $\text{MgOHOCOOCH}_3$ ;
- Upon mild heating (50-70 °C) of  $\text{Mg}_x\text{CO}_y \cdot \text{CH}_3\text{OH}$ , produced from  $\text{MgOHOCOOCH}_3$  in methanol, a micro- and/or mesoporous  $\text{Mg}_x\text{CO}_y$  is formed;

- It is currently believed that the evaporating gases, alcohol of crystallization and CO<sub>2</sub> gas trapped in the solvent, from the gel phase of Mg<sub>x</sub>CO<sub>y</sub>·CH<sub>3</sub>OH act as templates around which the solidification of Mg<sub>x</sub>CO<sub>y</sub> occurs;
- The reaction of micro- and/or mesoporous Mg<sub>x</sub>CO<sub>y</sub> formation is facilitated by mildly  
5 pressurizing the reaction vessel whereas the mere bubbling of CO<sub>2</sub> gas through the reaction medium does not produce the desired product. Under mild pressure conditions a gel phase is formed which is believed to be beneficial for the properties of the final product.
- It is further believed to be beneficial to heat the solution of MgO in CH<sub>3</sub>OH prior to or  
10 during pressurizing at 40-70 °C.

The method according to the invention forming the amorphous magnesium carbonate comprises the formation of a liquid or gel, and their subsequent solidification to form a powder or any other solid state mass. Gels may be obtained from the liquids by allowing the liquid to form a gel using any of the following methods, but not limited to, prolonged reaction  
15 time, adjustment of the temperature and/or pressure, or changing any other condition obvious for a person skilled in the art that forces the liquid to turn into a gel. The solid magnesium carbonate of the present invention is further obtained by solidification and subsequent drying of the gel or liquid at atmospheric, above-atmospheric or below-atmospheric pressure. Non limiting examples of solidification/drying processes include tray-drying, vacuum drying,  
20 spray-drying, freeze-drying, spray-freeze-drying, supercritical drying or any other known industrial or otherwise feasible drying process at temperatures below 350 °C, i.e. the temperature of magnesium carbonate decomposition. The solidification and drying of the gel or liquid results in a coarse solid mass that can be ground or similarly transformed into a fine powder.

*Experimental**Synthesis of the liquids:*

The amorphous magnesium carbonate according to the present invention are formed starting from opaque or translucent liquids formed in a reaction between one or several magnesium containing compounds (chosen from  $\text{MgO}$ ,  $\text{Mg}(\text{OH})_2$  and/or any of their respective Mg containing alcoxides chosen from alcohols, having a generic formula of  $\text{R-OH}$  in which R is any aliphatic or aromatic group, subject to limitations shown in examples below) with pressurized (above atmospheric pressure) carbon dioxide (or any other compound which can serve as the source of it) in an organic solvent, wherein one of the components is preferably but not necessarily alcohol. Non-limiting examples of alcohols include methanol, ethanol, n-propanol, isopropanol, butyl alcohol, pentanol, hexanol, heptanol, octanol, ethylene glycol, glycerine, phenol, or benzoyl alcohol. Optionally, water may form in situ during reaction or may optionally be added to facilitate the reaction in quantities between 0 and 10 vol %. Non limiting examples of additional organic solvent components, which can be both water miscible and immiscible, include acetone, acetonitrile, benzole, chloroform, dichlormethane, diethylether, diisopropylether, dimethylformamide, dioxane, methylesther of acetic acid, ethylesther of acetic acid, n-hexane, cyclohexane, dimethylsulfoxide, pyridine, tetrahydrofurane, toluol, or xylol. Non-Mg containing compounds may optionally be part of the reaction in quantities not exceeding the weight of the Mg-containing compound. Non limiting examples of such materials include  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{BaCO}_3$ ,  $\text{ZnCO}_3$ ,  $\text{Al}_2(\text{CO}_3)_3$ ,  $\text{SrO}$ ,  $\text{BaO}$ ,  $\text{CaO}$ ,  $\text{ZnO}$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$  and  $\text{SiO}_2$  and/or any of their respective alcoxides with alcohols having a generic formula of  $\text{R-OH}$ , wherein R is any aliphatic or aromatic group.

In a further embodiment one type of liquid is formed in a reaction between MgO and carbon dioxide (at above atmospheric pressure) in a reaction medium in which one of the components is an organic solvent, more preferably alcohol.

In one embodiment one type of liquid is formed in a reaction between Mg alcoxide and carbon dioxide at above-atmospheric pressure in which the reaction medium is an organic solvent, which may or not be water miscible, more preferably alcohol.

In yet another embodiment one type of liquid is formed in a reaction between Mg containing compound and carbon dioxide at above-atmospheric pressure in which the reaction medium is methanol.

10 In yet another embodiment one type of liquid is formed in a reaction between Mg containing compound and carbon dioxide at above-atmospheric pressure in which the reaction medium is a mixture between alcohol and another organic solvent, which may or not be water miscible. No limiting example of organic solvent includes acetone, acetonitrile, benzole, chloroform, dichlormethane, diethylether, diisopropylether, dimethylformamide, dioxane, methylesther of acetic acid, ethylesther of acetic acid, n-hexane, cyclohexane, dimethylsulfoxide, pyridine, tetrahydrofurane, toluol, or xylol.

*Synthesis of gels:*

In one embodiment of the invention, gels are formed from the liquid by allowing the liquid to harden into a gel. This can be obtained via methods such as, but not limited to, prolonged reaction time, adjustment of the temperature and/or pressure, or changing any other condition that forces the liquid to turn into a gel.

*Synthesis, solid material:*

One embodiment of the present invention results in a solid material formed by solidification and subsequent drying of the gel or liquid at atmospheric, above-atmospheric or below-atmospheric pressure. Non limiting examples of solidification/drying processes include tray-drying, vacuum drying, spray-drying, freeze-drying, spray-freeze-drying, supercritical drying  
5 or any other known industrial or otherwise feasible drying process at temperatures below 350 °C, i.e. the temperature of magnesium carbonate decomposition.

One embodiment of the present invention includes one type of powder formed by spray-drying the liquid having set the outlet temperature of the spray-dryer above the boiling point  
10 of the organic solvent or the mixture thereof used to produce the liquid, while the inlet temperature is set above the outlet temperature of the spray-dryer.

*Synthesis, film and coating:*

One embodiment of the present invention includes coherent films or coatings formed by solidification and subsequent drying of the gel or liquid applied to a surface at atmospheric,  
15 above-atmospheric or below-atmospheric pressure. Non limiting examples of solidification/drying processes include tray-drying, vacuum drying, freeze-drying, spray-freeze-drying, supercritical drying or any other known industrial or otherwise feasible drying process at temperatures below 350 °C, i.e. the temperature of Magnesium carbonate decomposition. The solidification and drying of the gel or liquid results in a coherent and  
20 solid film or coating.

*Synthesis, dried powder:*

One embodiment of the present invention includes providing dried powder which is formed in any of the ways described above and subsequently heat-treated at temperatures below 350 °C for 10 minutes or longer.

*Mixtures:*

In one aspect of the invention the amorphous magnesium carbonate is introduced as part of a composite, composition, mixture, formulation or other system (hereafter referred to as a composite) into which the amorphous magnesium carbonate may be incorporated using various methods included, but not limited to, mixing, spray drying, molding, or other feasible method of making a composite. The purpose of introducing the amorphous magnesium carbonate according to the invention in such composite could be any, including, but not limited to improving the functionality or introduction new functionality to a composite in e.g. water sorption processes.

10 *Surface coatings:*

In one embodiment of the invention, the amorphous magnesium carbonate is used in surface coatings alone or as part of a composite as described above. The surface coating can be deposited on any substrate through surface deposition techniques such as, but not limited to, spin coating and electrophoretic deposition. The rationale for using the amorphous magnesium carbonate in a surface coating could be, but is not limited to, to improve and/or add functionality to a product

The synthesis of the materials can be divided into three steps as described below:

[Step 1] Mixing a Mg-containing precursor and an alcohol-containing liquid in a reactor, examples of possible ingredients are discussed above. The mixing is preferably performed under stirring and the consistency of the mixture is preferably of liquid character. During this step, the ingredients in the mixture react to form one or several intermediates that later can interact with CO<sub>2</sub>. The mixture is preferably heated in order to facilitate reactions between the ingredients in the mixture. The reactor can also be pressurized to facilitate reaction between the ingredients or

control the boiling temperature of the alcohol-containing liquid. Temperatures between 40°C and boiling temperature of the liquid are preferable for the reaction to occur, however lower temperatures down to the freezing temperature of the liquid is enough for a less complete reaction. This step typically takes about 3h to 24h at 50°C for liquid volumes of 100 to 3000ml. Generally, a slightly yellow (transparent to opaque) liquid product is formed during this step. Higher temperatures reduce the time needed for reaction to take place. The CO<sub>2</sub> pressure during this step can range from 0.001 to 200bar above atmospheric pressure, however pressures below 10bar are preferable.

**[Step 2]** Reacting the mixture with CO<sub>2</sub>. In this step, the intermediate products formed during step 1 interact with CO<sub>2</sub> to form one or several types of carbonated intermediate products. The reaction is preferably performed under stirring to facilitate reaction. This step can be performed at temperatures ranging from the freezing temperature to the boiling temperature of the liquid, and at CO<sub>2</sub> pressures ranging from 0.001 to 200 bar above atmospheric pressure. However, temperatures below 50°C and pressures below 5 bar are beneficial for carbonation of the intermediate products. During this step, the carbonated intermediate products can form a gel in the reactor, typically this occurs after 4-6 days if the CO<sub>2</sub> pressure is 1 bar and the temperature is 20 °C during step 2. Increasing the pressure or adjusting the temperature can result in faster gel formation. However, the gel formation is not crucial for formation of the final magnesium carbonate in step 3. Generally step 2 takes 1-5 days, longer reaction times result in a higher yield of magnesium carbonate in the final material obtained in step 3.

[Step 3] Solidification and drying of the material. In this step, the liquid or gel formed in the reactor during step 2 is dried in order to obtain a solid material. During this step, the carbonated intermediate products formed during step 2 are transformed into anhydrous magnesium carbonate. A solidification of the material is associated with this drying process and the transformation to magnesium carbonate is facilitated when the products from step 2 are dried at temperatures between 60 °C and 300 °C. However, the transformation to magnesium carbonate also occurs at lower temperatures but can take up to several weeks if the drying is performed at room temperature. Depending on the intermediates formed during step 1 and 2, presence of water during step 3 could facilitate the transformation to magnesium carbonate via hydrolysis. After complete transformation of the intermediate products formed in step 2 to magnesium carbonate, traces of unreacted Mg-containing precursor material can reside in the final product. Careful considerations regarding the conditions during step 1 and 2 can minimize the amount of unreacted precursor material in the final product. The drying and solidification process in step 3 can include techniques such as spray drying or oven drying.

*Specific example:*

In a preferred embodiment of the invention MgO is used as the Mg-precursor and methanol (CH<sub>3</sub>OH) as the alcohol and the steps of the method comprise:

[Step 1] Mixing a Mg-containing precursor and an alcohol-containing liquid:

MgO (e.g. 4 g) and methanol (CH<sub>3</sub>OH) (e.g. 60 ml) are mixed, the suspension is heated to between 50 °C and 70 °C for 3-4 hours to form the intermediate Mg(OH)(OCH<sub>3</sub>), most preferably to 50 °C. The solution is continuously stirred



during this step.

**[Step 2]** Reacting the mixture with CO<sub>2</sub>:

5 The solution, now containing Mg(OH)(OCH<sub>3</sub>), is pressurized with 1-3 bar above atmospheric pressure CO<sub>2</sub> to form the intermediate Mg(OCO)(OCH<sub>3</sub>)<sub>2</sub> and/or Mg(OCO)(OCH<sub>3</sub>)(OH). The CO<sub>2</sub> pressure can be applied during step 1 as well, i.e. when MgO and methanol is mixed. At this point the temperature is between room temperature (i.e. 25 °C) and up to about 55 °C. The solution is continuously stirred during this step. Higher temperatures decreases the solubility of CO<sub>2</sub> in the liquid, which is negative for the reaction since CO<sub>2</sub> is needed not only to form the intermediates described above, but also since extra CO<sub>2</sub> will dissolve in the liquid and physically bond to the same intermediates. CO<sub>2</sub> dissolved in the liquid and CO<sub>2</sub> physically bonded to the Mg(OCO)(OCH<sub>3</sub>)<sub>2</sub> and/or Mg(OCO)(OCH<sub>3</sub>)(OH) is responsible for the formation of the micropores in the material when it is released as gas upon depressurization of the reaction vessel and then causes an expansion of the material. Hence, pressure and an excess of CO<sub>2</sub> is needed during this step for the later formation of pores in material, i.e. for a complete transformation of MgO to MgCO<sub>3</sub> and also formation of micropores, the CO<sub>2</sub>:MgO molar ratio needs to be higher than 1:1. This reaction step where Mg(OCO)(OCH<sub>3</sub>)<sub>2</sub> and/or Mg(OCO)(OCH<sub>3</sub>)(OH) is formed continues for approximately 2-4 days. A higher temperature and pressure leads to a faster gel formation but also to a less complete reaction.

**A) Depressurizing:**

25 After 3-4 days the reaction vessel is depressurized, the depressurization is done fast,

i.e., within minutes. It is at this point the micropores in the material are formed when the dissolved and physically bound CO<sub>2</sub> is released as described above. To allow the liquid/gel to expand upon release of CO<sub>2</sub>, the pressure of the CO<sub>2</sub> gas is reduced to atmospheric pressure, i.e. from 1 to 0 bar above atmospheric pressure, in the reactor and at the same time the temperature is increased to 70-100 °C in order to decrease the solubility of the CO<sub>2</sub> in the liquid/gel and to solidify the material. If the material is in the form of a liquid at this point it turns into a gel in a matter of minutes when the temperature is raised and the solution is depressurized. A visible swelling of the gel can be observed at this time before the material solidifies completely. At this point, a temperature at or above 70 °C is recommended in order to solidify the material rapidly since this will conserve the micropores in the material, a low temperature at this stage will produce a material with a lesser amount of micropores.

#### B) Drying:

To dry the material a furnace, rotary evaporator or other drying equipment can be used. During the drying of the material the mean pore size increases a bit (from approximately 3 nm up to about 7 nm). When the material is being dried the organic groups that remains in the material from the synthesis are being released which is what causes the pore size increase. For a complete removal of the organic groups (i.e. a “pure” material) drying above 250 °C is needed, the purity of the material is increased with the drying temperature.

To analyze the material synthesised in the specific example the following methods and equipment may preferably be used:

Nitrogen sorption measurements can be carried out at 77 K using an ASAP 2020 from Micromeritics. The samples are degassed at 95 °C under vacuum for 10 h prior to analysis with a vacuum set point of 10 µm Hg. The specific surface area (SSA) are determined by applying the 5 point Brunauer-Emmet-Teller (BET) equation (Brunauer S, Emmet PH, Teller E, *J Am Chem Soc*, 1938, 60:309) to the relative pressure range 0.05-0.30 of the adsorption branch of the isotherm. The pore size distribution are determined using the DFT method carried out with the DFT Plus software from Micromeritics using the model for nitrogen adsorption at 77 K for slit-shape geometry with no-negative regularization and high smoothing ( $\lambda=0.02000$ ).

10 X-ray diffraction (XRD) analysis can be performed with a Bruker D8 TwinTwin instrument using Cu-K $\alpha$  radiation. Samples are ground and put on a silicon zero background sample holder prior to analysis. The instrument are set to operate at 45 kV and 40 mA. Analyses of the diffractogram can be performed using the software EVA V2.0 from Bruker.

Infrared spectroscopy (FTIR) can be performed with a Bruker Tensor27 instrument using a  
15 Platinum ATR diamond cell. A background scan are recorded prior to the measurement and subtracted from the sample spectrum, 32 scans are signal-averaged for each spectrum.

The effects of drying at an elevated temperature is shown in figure 30 where the Evolved gas evolution (EGA) data from a representative sample of the magnesium carbonate according to the invention is shown. EGA detects the decomposition products from a material, and in  
20 figure 30 it can be seen that between 100-250 °C CO<sub>2</sub> and H<sub>2</sub>O is detected. This is due to remaining -OH and -OCH<sub>3</sub> groups in the material, above 250 °C the carbonate decomposes which can be seen by the massive formation of CO<sub>2</sub> above this temperature. Figure 31 shows the growth in pore size at different time points for a material stored at 70 °C and also calcined at 300 °C, associated with decomposition of the organic groups. The pore size distribution for

the as-synthesised material (triangle), which is the material directly after step 3B above that has been dried at 70 °C, the same material stored for 1 (circle) and 3 (star) months at 70 °C and the same material that has been calcined (square), i.e. dried at 300 °C, are shown. Table 1 displays the pore volume and surface areas associated with the increased pore size due to decomposition of the organic groups.

**Table 1.** Representative values for specific surface area (SSA), pore volume and mean pore widths for the material after different storage conditions, as measured using nitrogen sorption

Sample	As-synthesized	1 month 70 °C air	3 months 70 °C air	Calcined 300 °C N <sub>2</sub>
SSA [m <sup>2</sup> /g] <sup>a</sup>	638 ± 5	397 ± 3	387 ± 2	265 ± 1
Total pore volume [cm <sup>3</sup> /g] <sup>b</sup>	0.36	0.50	0.51	0.42
DFT Pore width [nm] <sup>c</sup>	2.5	4.7	5.0	5.5
Limiting micropore volume [cm <sup>3</sup> /g] <sup>d</sup>	0.21 ± 0.00	0.13 ± 0.00	0.13 ± 0.00	0.10 ± 0.00

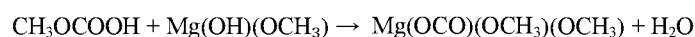
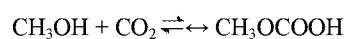
<sup>a</sup> Established with the BET equation, using 5 points in the relative pressure range from 0.05 to 0.3

10 <sup>b</sup> Single point adsorption at  $P/P_0 \approx 1$

<sup>c</sup> Established by DFT analysis of the nitrogen adsorption isotherm

<sup>d</sup> According to the D-A equation, the divergence for all the values are less than 0.001

The understood reaction mechanisms in the preferred embodiment as described above are:





In another laboratory experiment the amorphous magnesium carbonate according to the invention is formed in a reaction between 120ml methanol and 8g MgO in a CO<sub>2</sub> atmosphere, leading to the formation of a gel, and subsequent solidification and drying of the obtained product. The initial temperature in the reaction vessel containing methanol and MgO is set to 50 °C and the CO<sub>2</sub> pressure is set to 3 bar (above atmospheric pressure). After 4h, the temperature is lowered to 25°C and the pressure is lowered to 1 bar (above atmospheric pressure) in the reaction vessel. After a couple of hours of reaction, the initially milky white suspension turns into an opaque or translucent yellowish liquid. After about 4 days, a gel formation occurs in the reaction vessel and the reaction is deliberately terminated by a gentle depressurization of the reaction vessel. The gel is subsequently transferred onto a tray and dried in an oven set to 70 °C which leads to a solidification and drying of the gel. In this particular case, the solidification process takes less than 1h while the drying process takes several days. After being dried, the solidified material is ground to a powder, using e.g. ball milling. It is obvious that one skilled in the art can choose from several available grinding processes such as mortar, impact, attrition, jet grinding or any other industrially suitable type. Alternatively the powder is heat-treated after the solidification and drying as described above prior to the grinding. After drying above 250 °C the powder obtained a surface area of 240 m<sup>2</sup>/g and a total pore volume of 0.42 cm<sup>3</sup>/g.

In further experiments the amorphous magnesium carbonate according to the invention is formed in a reaction between 120ml methanol and 8g MgO in a CO<sub>2</sub> atmosphere, leading to formation of a liquid and subsequent solidification and drying of the obtained product. The initial temperature in the reaction vessel methanol and MgO is set to 50 °C and the CO<sub>2</sub> pressure is set to 3 bar (above atmospheric pressure). After 4h, the temperature is lowered to 25°C and the pressure is lowered to 1 bar (above atmospheric pressure) in the reaction vessel.

After a couple of hours of reaction, the initially milky white suspension turns into a slightly yellow liquid. After 2 days, the reaction is deliberately terminated by a gentle depressurization of the reaction vessel. The liquid is subsequently transferred to a tray and dried in an oven set to 70°C which leads to a solidification and drying of the liquid. In this particular case, the solidification process takes less than 1h while the drying process takes several days. After being dried, the solidified material is ground to a powder, using e.g. ball milling. It is obvious that one skilled in the art can choose from several available grinding processing such as mortar, impact, attrition, jet grinding or any other industrially suitable type. Alternatively the powder is heat-treated after the solidification and drying as described above prior to the grinding.

Currently preferred materials to start the reaction of forming the amorphous magnesium carbonate include MgO, CO<sub>2</sub> and an alcohol, such as e.g. methanol.

Two aspects of the method of synthesizing the amorphous magnesium carbonate according to the invention deserve further discussion. If CO<sub>2</sub> is merely passed (bubbled) through a methanolic suspension of MgO or another magnesium containing material at atmospheric pressure, no reaction is observed. During the development of the particular amorphous magnesium carbonate materials, we surprisingly found that moderately pressurized CO<sub>2</sub> gas (preferentially ~1-3 bar above atmospheric pressure or higher) in a sealed container saturated with CO<sub>2</sub> converts MgO to anhydrous magnesium carbonate in methanol. Nothing in the previous art has suggested that (a) anhydrous magnesium carbonate can be produced in alcoholic suspensions and (b) that moderate pressure will be most favorable to produce the desired effect. On the contrary, earlier teachings suggested that Magnesium carbonate cannot be obtained from methanolic suspensions, unlike the carbonates of Ca, Ba and Sr. We have also further observed that CO<sub>2</sub> pressure in the reaction vessel has a drastic impact on the gelation time, which is decreased threefold when the pressure is kept at 3 bar over

atmospheric pressure throughout the reaction. We have also observed that the excessive pressure may also result in a lower yield of magnesium carbonate in the final product and produce more traces of unreacted MgO.

*Examples*

5   EXAMPLE 1

MgO	8 g
Methanol	120 ml
CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

- 10   8g MgO powder was placed in a glass bottle together with 120 ml methanol and a stirring magnet. The solution was put under 3 bar above atmospheric pressure CO<sub>2</sub> pressure and heated to 50°C. After approximately 3 hours the mixture was allowed to cool to room temperature and the CO<sub>2</sub> pressure was lowered to 1 bar above atmospheric pressure. The initially milky white suspension in the reaction vessel transformed gradually into a slightly
- 15   yellowish liquid in the reaction vessel after a couple of hours. The reaction continued for about 4 days until a gel had formed in the reaction vessel. Subsequently the pressure in the reaction vessel was brought to atmospheric pressure and the gel was collected and put onto a tray for drying in an oven at 70 °C. The latter caused the gel to solidify within an hour. The solidified material was left in the oven to dry for 2 days.

20   Material characterization, example 1

The dried material formed a coarse powder that was primarily amorphous with traces of unreacted and crystalline MgO, see X-Ray Diffraction (XRD) pattern in Fig. 1. The sharp peaks at 43° and 62° 2θ originate from the unreacted MgO while the halo peak between 25° and 40° 2θ is indicative of at least one amorphous phase.

Raman spectroscopy reveals that the powder is indeed composed of magnesium carbonate, see Fig. 2, where the band at  $\sim 1100\text{ cm}^{-1}$  corresponds to vibration of the carbonate group. Moreover, a broad halo, or the so-called Boson peak, with a maximum at  $\sim 100\text{ cm}^{-1}$  further witnesses of the amorphous character of the powder.

- 5 When examined with Fourier transform infrared spectroscopy (FTIR), see Fig. 10, the material shows absorption bands at  $\sim 1440\text{ cm}^{-1}$ ,  $\sim 1100\text{ cm}^{-1}$  and  $\sim 850\text{ cm}^{-1}$  which all correspond to the carbonate group. No water of crystallization is visible in this spectrum.

The anhydrous character of the bulk material is further confirmed by Thermal Gravimetric Analysis (TGA), see Fig 3, where the loss with a maximum at  $150\text{ }^{\circ}\text{C}$  is due to loss of  
10 remaining organic groups. X-ray photoelectron spectroscopy (XPS) confirms the anhydrous nature of the magnesium carbonate: Energy resolved spectra were recorded for the  $\text{Mg}_{2p}$  and  $\text{O}_{1s}$  peaks, see Figs. 9 and 11. The position of the  $\text{Mg}_{2p}$  peak at  $52.1\text{ eV}$  and  $\text{O}_{1s}$  peak at  $533.5\text{ eV}$  are indicative of magnesium carbonate, and the  $\text{O}_{1s}$  peak does not contain any components for crystal water, which otherwise would have appeared at  $533\text{--}533.5\text{ eV}$ . The shoulder seen  
15 at  $535.6\text{ eV}$  is located between the binding energies for liquid water ( $539\text{ eV}$ ) and ice ( $533\text{ eV}$ ) and hence is representative for surface adsorbed water as previously described for surface adsorbed water on carbon fibers. The shoulder seen at  $531.0\text{ eV}$  shows the presence of  $\text{MgO}$  in the powder. No presence of  $\text{Mg}(\text{OH})_2$  was observed in the bulk which, expectedly, would have resulted in a peak at  $532.4\text{ eV}$ .

- 20 In order to analyze the pore structure and water sorption capacity of the produced amorphous magnesium carbonate according to the present invention,  $\text{N}_2$  and  $\text{H}_2\text{O}$  vapor sorption analyses were carried out. Figure 6 shows the  $\text{N}_2$  sorption isotherm for the magnesium carbonate according to the present invention and displays a typical Type 1 shape of the isotherm according to the IUPAC classification, which is indicative of a microporous adsorbent. The



lack of hysteresis between the adsorption and desorption branches in the  $N_2$  isotherm is a distinct feature for microporous. Figure 5 shows the isotherm for  $H_2O$  vapor adsorbed on the magnesium carbonate according to the present invention, which provides information about the materials interaction with water molecules.

- 5 Based on the massive  $H_2O$  vapor adsorption at low RHs, it is evident that the produced amorphous magnesium carbonate material, according to the present invention, strongly interacts with water molecules and shows a strong hydrophilic behavior. The limited amount of desorption from the material when the RH is reduced from ~95 % to ~5 % is further proof of the strong interaction between water molecules and the amorphous magnesium carbonate
- 10 according to the present invention. It should, however, be noted that no signs of hydrate formation of the material is seen using XRD after the isotherm is completed and that the isotherm can be repeated with similar result after heat treatment of the magnesium carbonate according to the present invention at moderate temperature (95 °C).

Both isotherms were analyzed further to establish both the specific surface area (SSA) of the

15 material according to the Brunauer-Emmet-Teller (BET) equation, and the micro-porous properties according to the Dubinin-Astakhov (D-A) model, see Table 2.

It should be noted that the total pore volume given in Table 2 refers to the total volume of pores filled with nitrogen gas at saturation pressure in a nitrogen sorption experiment carried out at 77 K. This is also the pore volume referred to elsewhere in the text when a pore volume

20 is given without reference to a specific pore size interval.

The hydrophilic nature of the material was further reflected in the greater characteristic energy for adsorption of  $H_2O$  compared to  $N_2$ . The discrepancy in limiting micro-pore volume ( $w_0$ ) - in which the value obtained from the  $N_2$  isotherm is that normally reported in the literature - and modal equivalent pore size obtained from the two isotherms is most likely due

to site-specific interaction between the H<sub>2</sub>O species and the material, not only in the micro-pores but also on the exterior of the material and in pores larger than 2 nm.

The SSA of the amorphous magnesium carbonate powder according to the present invention is observed to be  $\sim 800 \text{ m}^2/\text{g}$  which is up to two orders of magnitude larger than corresponding values reported for any other form of magnesium carbonate, with commercial (crystalline) analogues typically having SSAs of about  $4\text{--}18 \text{ m}^2 \text{ g}^{-1}$ . For previously reported amorphous magnesium carbonate produced by thermal decomposition of hydrated magnesium carbonate forms, the highest SSA found in the literature is  $\sim 50 \text{ m}^2 \text{ g}^{-1}$ . In fact, the SSA observed for the amorphous magnesium carbonate according to the present inventions is extraordinarily high, not only for magnesium carbonate, but also for alkaline earth carbonates and minerals in general. This places the amorphous magnesium carbonate according to the present invention in the exclusive class of high surface area nanomaterials including meso-porous silica, zeolites, metal organic frameworks (MOFs), and carbon nanotubes.

Table 2. Structural and chemical characteristics of the amorphous magnesium carbonate according to the present invention obtained from N<sub>2</sub> and H<sub>2</sub>O vapor isotherms.

Adsorbate	N <sub>2</sub>	H <sub>2</sub> O
SSA <sup>1</sup> (m <sup>2</sup> /g)	800 ± 3.60	-
Total pore volume (cm <sup>3</sup> /g)	0.47	-
w <sub>0</sub> , limiting micropore volume <sup>3</sup> (cm <sup>3</sup> /g)	0.28 ± 0.000559	0.16 ± 0.0102
Equivalent surface area in micropores <sup>3</sup> (m <sup>2</sup> /g)	549	478
Characteristic energy of adsorption <sup>3</sup> (kJ/mol)	11.4	41.0
Modal equivalent pore width <sup>3</sup> (nm)	1.75	1.09
Correlation coefficient of fit <sup>3</sup>	0.999	0.977

<sup>1</sup> According to the 5-point BET equation applied in the relative pressure range from 0.05 to 0.3

<sup>2</sup> Single point adsorption at P/P<sub>0</sub> ≈ 1

<sup>3</sup> According to the Dubinin-Astakhov equation

The pore size distribution (see Fig 8) of the sample was evaluated using the DFT Plus software from Micromeritics using the model for nitrogen at 77 K on carbon with slit-shaped pores. The DFT-based cumulative pore size distribution gives that about 98 % of the pore volume is constituted by pores with a diameter smaller than 6 nm while the remaining pore volume is made up of pores with a broad size distribution between 8 and 80 nm centered around 16 nm. As can be seen in Fig. 8 the cumulative pore volume of pores with a diameter smaller than 10 nm is above 0.40 cm<sup>3</sup>/g. When examined with scanning electron microscopy (SEM), these larger pores are clearly visible in some parts of the material as illustrated in Fig. 12. These larger pores are, however, not visible throughout the entire material, which is consistent with the limited contribution to the total pore volume from such pores.

The water sorption capacity of the material is interesting from an industrial and technological point of view and it is, hence, compared to three commercially available desiccants, viz. fumed silica (SSA: 196 m<sup>2</sup> g<sup>-1</sup>), hydromagnesite (SSA: 38 m<sup>2</sup> g<sup>-1</sup>) and the micro-porous Zeolite Y (SSA: 600 m<sup>2</sup> g<sup>-1</sup>, silica/alumina ratio 5.2:1), see Fig. 5. The H<sub>2</sub>O vapor adsorption isotherm for the amorphous magnesium carbonate according to the present invention displays similarities with the hydrophilic zeolite at very low RHs (< 1 %) and shows on an even higher adsorption capacity for the amorphous magnesium carbonate according to the present invention compared to the zeolite at RHs between 1 and 60 %. This behaviour contrasts largely to that of the other two non-porous materials that mainly adsorb H<sub>2</sub>O at RH > 60%. The H<sub>2</sub>O vapor adsorption behavior for the amorphous magnesium carbonate according to the present invention was also studied by dynamic vapor sorption (DVS) which confirmed that the material has an extraordinary capacity to adsorb H<sub>2</sub>O vapor, even at extremely low RH, a property highly desirable for desiccants in various applications. Heating the sample to 95°C appeared to regenerate the water sorption capacity without any crystal phase changes.

The characterization described above was utilized, at least partly, for the examples described below.

#### EXAMPLE 2

5 As described in Example 1 but where the obtained powder was heat-treated at 70°C for 7 days. The particles proved to be composed of a material similar to the one in Example 1, viz. amorphous and anhydrous magnesium carbonate with traces of MgO. However, the specific surface area proved to be 454 m<sup>2</sup>/g, with a distinct pore size distribution around 6 nm. As can be seen in Fig. 14 the cumulative pore volume of pores with a diameter smaller than 10 nm is  
10 above 0.7 cm<sup>3</sup>/g. The nitrogen sorption isotherm and the pore size distribution obtained via DFT analysis of the nitrogen isotherm for this sample is displayed in Fig. 13 and 14, respectively. This well-defined pore size distribution is similar to those found in ordered mesoporous silica materials and seldom found elsewhere. Also this material was associated with a H<sub>2</sub>O vapor sorption isotherm similar to the one described in Example 1.

15

#### EXAMPLE 3

As described in Example 1 but where the liquid was spray-dried before a gel was formed in the reaction vessel.

20 The liquid obtained after the reaction between MgO and methanol transformed into particles when spray-dried. The particles proved to be composed of a material similar to the one in Example 1, viz. amorphous magnesium carbonate with traces of MgO. The average particle size was approximately 1 µm in diameter as determined by SEM analysis, SEM image in Fig. 15. The surface area of the obtained particles was 68.5 m<sup>2</sup>/g as determined by BET analysis.

The water vapor sorption of the spray-dried material at different RH ranging from 0-100 % is displayed in Fig. 16. As can be seen in Fig. 17 the cumulative pore volume of pores with a diameter smaller than 10 nm is above 0.018 cm<sup>3</sup>/g. The nitrogen sorption isotherm for the magnesium carbonate of the present invention in this example is displayed in Figure 18.

- 5 When 0.8g dried magnesium carbonate of the present invention produced in this example was put in a sealed chamber with 100% RH at room temperature, the weight of the sample increased to 2.2g by adsorption and uptake of water within 48h as displayed in Fig. 20. The material continued to gain weight for several days.

#### 10 EXAMPLE 4

As described in Example 1 but with the material prepared with ethanol instead of methanol

MgO	8 g
Ethanol	120 ml
CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

15

- The attempt with ethanol as solvent did not result in any visible gel formation in the reaction vessel. However, when the liquid was placed in an oven set to  $\leq 70^{\circ}\text{C}$ , it formed a gel that solidified and later transformed into a powder when dried. This powder contained large amounts of unreacted MgO, but it also shared some the characteristics of the previously prepared powders in Example 1. It also contained magnesium carbonate, which is suggested to be the reason for the solidification of the ethanolic liquid once placed in the oven as verified with XRD. Surprisingly, the surface area of this material was 737 m<sup>2</sup>/g, which is in agreement to the magnesium carbonate produced with methanol.
- 20

After several weeks in the reaction vessel (at room temperature and atmospheric pressure) a clear gel formed at the top of the vessel. The clear gel also consisted of amorphous magnesium carbonate without traces of MgO as characterized by XRD and FT-IR. The surface area of this material is 225 m<sup>2</sup>/g and a pore volume of 1.55 cm<sup>3</sup>/g. The pore volume for pores less than 10 nm in width is 0.8 cm<sup>3</sup>/g, see Figure 19.

#### EXAMPLE 5

As described in Example 1 but prepared with addition of toluene.

	MgO	8 g
10	Methanol	46 ml
	Toluene	74 ml
	CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

The toluene accelerated the formation of magnesium carbonate in the present example where the gelation time was reduced compared to when only methanol was used, however the surface area of the obtained material was in this case 222 m<sup>2</sup>/g and the pore volume was 0.78 cm<sup>3</sup>/g with a broader pore size distribution ranging from approximately 4 nm diameter to 30 nm, with a maximum at 10 nm. The volume of pores with a diameter less than 10 nm is 0.36 cm<sup>3</sup>/g, see Figure 21.

#### EXAMPLE 6

As described in Example 1 but with a higher amount of methanol, and gel formation through increased temperature. After 4 days of reaction, the temperature in the reaction vessel was increased to 30 °C which caused the liquid to turn into a gel.

MgO	8 g
Methanol	140 ml
CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

- 5 The obtained amorphous magnesium carbonate according to the present invention proved to be composed of anhydrous and amorphous magnesium carbonate and crystalline MgO as in Example 1. The magnesium carbonate according to the present invention in this example had a surface area of 400 m<sup>2</sup>/g, a pore volume of 0.97 cm<sup>3</sup>/g and a narrow pore size distribution around 8 nm. The volume of pores with a pore diameter less than 10 nm is 0.91 cm<sup>3</sup>/g, see  
10 Figure 22.

#### EXAMPLE 7

As described in Example 1 but with a higher synthesis pressure.

MgO	8 g
15 Methanol	120 ml
CO <sub>2</sub> (gas)	3 bar (above atmospheric pressure)

- In this experiment, the gas pressure was kept a 3 bar until a gel had formed in the reaction vessel. This led to a faster reaction (3 times faster) as compared to Example 1. The obtained  
20 material proved once more to consist of amorphous and anhydrous magnesium carbonate with traces of MgO as described in Example 1. The surface area measured via gas adsorption for the material obtained in this experiment was 309 m<sup>2</sup>/g with a pore volume of 0.575 cm<sup>3</sup>/g. The DFT-based pore size distribution showed pore diameters between 4-8 nm, with a maximum around 6nm. The volume of pores with diameter less than 10 nm is 0.53 cm<sup>3</sup>/g, see  
25 Figure 23.

## EXAMPLE 8

As described in Example 1 but with a lower amount of MgO, and gel formation through increased temperature. After 4 days of reaction, the temperature in the reaction vessel was increased to 40 °C which caused the liquid to turn into a gel.

MgO	6 g
Methanol	120 ml
CO <sub>2</sub> (gas)	1 bar & 3 bar (above atmospheric pressure)

- The obtained magnesium carbonate according to the present invention proved to be composed of anhydrous and amorphous magnesium carbonate and crystalline MgO as in Example 1. The surface area of the obtained material was 284 m<sup>2</sup>/g with a total pore volume of 0.93 cm<sup>3</sup>/g and a narrow pore size distribution around 8.5 nm. The volume of pores with diameter less than 10 nm is 0.54 cm<sup>3</sup>/g, see Fig 24.

## EXAMPLE 9

As described in Example 1 but with a lower synthesis temperature.

MgO	8 g
Methanol	120 ml
CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

In this experiment, the reaction temperature was kept at room temperature until a gel had formed in the reaction vessel. This led to a significantly slower reaction as compared to Example 1. The obtained material proved once more to consist of amorphous and anhydrous



magnesium carbonate with traces of MgO as described in Example 1 with similar characteristics.

#### EXAMPLE 10

- 5 As described in Example 1 but with addition of various amounts of CaO.

MgO/Ca(OH) <sub>2</sub> ratio	1:1 – 1:0 (8 g)
Methanol	120 ml
CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

- 10 Increasing amounts of Ca(OH)<sub>2</sub> in the powder phase prior to the reaction led to increasing amounts of amorphous CaCO<sub>3</sub> in the resultant material. Storing the materials at high relative humidities for an extended time crystallized the amorphous CaCO<sub>3</sub> content in the amorphous magnesium carbonate according to the present inventions. Amorphous and anhydrous magnesium carbonate was still obtained throughout the experiments.
- 15 When prepared with 5wt % Ca(OH)<sub>2</sub> in the powder phase, the surface area of the material of the present invention was 570 m<sup>2</sup>/g, with a total pore volume 0.63 cm<sup>3</sup>/g and a narrow pore size distribution around 4.5 nm. The volume of pores with diameter less than 10 nm is 0.58 cm<sup>3</sup>/g, see Fig. 25.

#### 20 EXAMPLE 11

As described in Example 1 but with addition of various amounts of SrO.

MgO/SrO ratio	1:1 – 1:0 (8 g)
Methanol	120 ml
CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

25

Increasing amounts of SrO in the powder phase prior to the reaction led to increasing amounts of crystalline  $\text{SrCO}_3$  in the resultant material. Amorphous and anhydrous magnesium carbonate was still obtained throughout the experiments.

#### 5 EXAMPLE 12

As described in Example 1 but with addition of various amounts of BaO.

MgO/BaO ratio	1:1 – 1:0 (8 g)
Methanol	120 ml
CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

10

Increasing amounts of BaO in the powder phase prior to the reaction led to increasing amounts of crystalline  $\text{BaCO}_3$  in the resultant material. Amorphous and anhydrous magnesium carbonate was still obtained throughout the experiments.

#### 15 EXAMPLE 13

As in example 3 but spin coated instead of spray dried.

The liquid was spin coated onto a silicon wafer and dried at 70 °C, which resulted in a coating of amorphous magnesium carbonate according to the present invention on the silicon wafer.

#### 20 EXAMPLE 14

As in Example 3 but where the liquid was filtered through a filter membrane having a pore size cut-off of at about 200 nm to obtain a clear, transparent liquid. The liquid was then stored at 1 bar (above atmospheric pressure) with CO<sub>2</sub> gas until a gel was formed. The gel was then transferred onto a tray and placed in an oven at 70 °C to solidify and dry. The obtained

product consisted of high purity anhydrous and amorphous magnesium carbonate of the present invention.

#### EXAMPLE 15

- 5 As described in Example 1 but where reaction vessel was depressurized before a gel had formed (after 3 days of reaction) and where the liquid was left in the vessel at room temperature and ambient conditions for 2 weeks before placed in an oven at 70 °C.

MgO	8 g
Methanol	120 ml
10 CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

- The liquid formed in the reaction vessel transformed into a gel when it was left standing for 24 at ambient conditions. When the gel was placed in the oven after 2 weeks it solidified and the material was dried out. This produced a solid material with the same composition as
- 15 described in Example 1, i.e. amorphous and anhydrous magnesium carbonate with traces of MgO. However, the SSA of the final material in this example was substantially lower (77 m<sup>2</sup>/g) as compared to the material in Example 1 and had a total pore volume of 0.47 cm<sup>3</sup>/g with a distinct pore size distribution around 20 nm, see figure 26 and 27. The pore volume corresponding to pores smaller than 10nm in diameter was only 0.0043 cm<sup>3</sup>/g in this example,
- 20 as illustrated in Fig. 27, which essentially corresponds to an absence of micro pores according to the definition used herein. The absence of micro pores and the low pore volume in the final material produced in this example caused a drastic decrease in water vapor sorption capacity as compared with the materials in Examples 1 and 2. The water sorption characteristics of the material in this example is displayed in Fig. 28.

## EXAMPLE 16

As described in Example 1 but with various temperatures and pressures during the initial stage of the synthesis reaction. The initial stage of the reaction is the time it takes for the slightly yellow liquid to form (approx. 3 hours in Example 1).

MgO	8 g
Methanol	120 ml
Initial reaction CO <sub>2</sub> pressure	0.001 bar to 79 bar (above atmospheric pressure)
10 Initial reaction temperature	From 0 °C to just below boiling temperature (max 100 °C)
Later reaction CO <sub>2</sub> pressure	1 bar (above atmospheric pressure)
Later reaction temperature	25 °C

- 15 The boiling temperature of methanol varies with pressure and hence the synthesis temperature in this example was adjusted so that the methanol never did boil at the current pressure. Increasing temperatures and pressures in the initial reaction stage resulted in faster formation of the slightly yellow liquid in the reaction vessel. At the lower temperatures and pressures, a change in color was not observed visually and the initial stage of the reaction was terminated
- 20 after 6 hours. A lower yield of magnesium carbonate was obtained in the final materials for the synthesis performed at low initial temperature and pressure.

## EXAMPLE 17

As described in Example 1 but with various temperatures and pressures during the later stage of the synthesis reaction. The later reaction stage is the phase of the reaction that follows when preferably the slightly yellow liquid has formed.

5	MgO	8 g
	Methanol	120 ml
	Initial reaction CO <sub>2</sub> pressure	3bar (above atmospheric pressure)
	Initial reaction temperature	50 °C
	Later reaction CO <sub>2</sub> pressure	0.001 bar to 79 bar (above atmospheric pressure)
10	Later reaction temperature	From 0 °C to below boiling (max 100 °C)

The boiling temperature of methanol varies with pressure and hence the synthesis temperature in this example was adjusted so that the methanol never did boil at the pressure used. The highest yield of magnesium carbonate in the final materials was obtained at pressures around  
 15 1 bar (above atmospheric pressure) and temperatures below 50 °C. However, various amounts of magnesium carbonate were obtained throughout the experiments.

#### EXAMPLE 18

As described in Example 1 but with higher temperatures during the solidification step.

20

	Methanol	120 ml
	CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)
	Solidification temperature	75 °C to 300 °C

25 This produced magnesium carbonate materials with similar characteristics as in Example 1.

## EXAMPLE 19

As described in Example 1 but with lower temperatures during the solidification step.

5	Methanol	120 ml
	CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)
	Solidification temperature	25 °C and below

This produced amorphous and low surface area materials.

10

## EXAMPLE 20

As described in Example 1 but below freezing temperature of methanol.

	MgO	8 g
15	Methanol	120 ml
	CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

In this case no reaction occurred.

## 20 EXAMPLE 21

As in Example 1 but prepared with pentane instead of methanol

	MgO	8 g
	Pentane	120 ml
25	CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

In this case no reaction occurred.

#### EXAMPLE 22

- 5 As described in Example 1 but with addition of various amounts of water

	MgO	8 g
	Methanol	120 ml
	H <sub>2</sub> O	5 - 100 ml
10	CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

In this case, crystalline phases of magnesium carbonates were formed. At higher water concentrations the resultant materials were hydrated while the materials formed at lower water concentrations were of more anhydrous nature.

15

#### EXAMPLE 23

As described in Example 1 but where the CO<sub>2</sub> was bubbled through the methanolic suspension of MgO.

	MgO	8 g
20	Methanol	120 ml

In this case no reaction occurred.

## EXAMPLE 24

As described in Example 1 but with 50 volumetric percent of water.

	MgO	8 g
5	Methanol	60 ml
	H <sub>2</sub> O	60 ml
	CO <sub>2</sub> (gas)	3 & 1 bar (above atmospheric pressure)

In this case, crystalline nesquehonite was formed, see figure 29. The material had a low  
 10 surface area and was non-porous and hence the presence of 60 ml water in 60 ml methanol  
 does not lead to the desired result.

## EXAMPLE 25

As described in Example 1 but with Mg(OH)<sub>2</sub> instead of MgO as the starting material.

	Mg(OH) <sub>2</sub>	8 g
15	Methanol	120 ml
	CO <sub>2</sub> (gas)	1 & 3 bar (above atmospheric pressure)

In this case no reaction occurred, hence the use of Mg(OH)<sub>2</sub> as a starting material when using  
 the same reaction conditions as in example 1 does not lead to the desired result.

## 20 EXAMPLE 26

As described in Example 1 but with Mg(OCH)<sub>3</sub> instead of MgO as the starting material.

	Mg(OCH) <sub>3</sub>	50 ml (10 wt% Mg(OCH <sub>3</sub> ) <sub>2</sub> in methanol)
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CO<sub>2</sub> (gas) 1 & 3 bar (above atmospheric pressure)

Water 0.87 ml

In this example the magnesium methoxide and water were placed in a reaction vessel under carbon dioxide pressure, the carbon dioxide pressure was set to 3 bar above atmospheric pressure for the first 3 hours and then lowered to 1 bar above atmospheric pressure for the remaining reaction time. The temperature was set to 50 °C for the first 3 hours and then room temperature for the remaining reaction time. The solution in the reaction vessel turned yellow within 1 hour and after 12 hours a powder had formed in the reaction vessel, this powder was characterized as magnesium methyl carbonate based on the IR spectra in fig 32. Hence in this example no magnesium carbonate was formed and therefore using these conditions Mg(OCH<sub>3</sub>)<sub>2</sub> is not a preferred starting material.

#### EXAMPLE 27

The magnesium carbonate material was prepared as in the specific example using a drying/calcination temperature of 250 °C. In this example the magnesium carbonate material and the zeolite Y material were dried at 250 °C over night, after this both the samples were placed in a desiccator saturated with water vapor, i.e. 100% relative humidity, at room temperature for 18 hours. After this the regeneration energy were compared between the two samples using a TGA instrument, more precisely a Thermogravimetric analyzer from Mettler Toledo, model TGA/SDTA851e instrument with a 3 °C/min ramping temperature was used. The measurements were performed under a flow of air. The result is shown in fig 33, as can be seen in the figure at 150 °C the magnesium carbonate material according to the present invention has lost 40wt% more water than the Zeolite Y and approximately 65 °C higher

temperature is needed for a complete removal of water in the zeolite Y material as compared to the magnesium carbonate material.

#### EXAMPLE 28

- 5 In this example the magnesium carbonate according to the current invention is used as a pharmaceutical excipient. As an illustrative example amorphous Ibuprofen was formulated using the magnesium carbonate according to the present invention.

##### *Introduction to Example 28*

- During the last decades, poor aqueous solubility of active pharmaceutical ingredients (APIs) has been one of the most challenging issues for the pharmaceutical industry. About 40% of newly marketed drugs have low solubility and 80-90% of drug candidates in the R&D pipeline fail due to solubility problems. Due to the poor aqueous solubility these drugs have low bioavailability and/or a slow onset of action, and this may lead to a limited and insufficient therapeutic effect. Therefore, much effort has been put into solving this issue using different types of strategies including salt formulations, API particle size reduction, use of solubilizers, solid dispersions, co-ground mixtures and pro-drugs. However, there are still practical limitations of these techniques. For example, the salt formation is available for acid and basic drugs, however it is not feasible for neutral compounds and it may be difficult to form salts of very weak bases and acids. Even if a stable salt can be formed, conversion from a salt to a poorly soluble free acid or base can occur both *in vitro* and *in vivo*; as to the particle size reduction, this method may lead to build-up of static charges and lead to handling difficulties. In this respect, preparation and stabilization of the API in its amorphous state have been suggested. Typically, organic polymers like polyethylene glycol (PEG) and polyvinyl pyrrolone (PVP) are used in solid dispersions for this purpose. However, this

approach suffers from the problems with chemical stability of products and difficulties in the industrial manufacturing processes. Recent developments in nanotechnology science have provided new inorganic materials that can be used to stabilize amorphous APIs. It has been found that mesoporous structures (pores with a diameter between 2 and 50nm) in materials  
5 have the ability to effectively suppress crystallisation of amorphous substances.

*Materials synthesis for Example 28*

Magnesium Oxide (MgO) and ibuprofen were obtained from Sigma-Aldrich, Sweden. Methanol and ethanol were purchased from VWR International, Sweden. CO<sub>2</sub> was obtained from Air Liquide, Sweden. All chemicals were used as received.

- 10 The magnesium carbonate was synthesised as follows: 170g of MgO and 2.5L CH<sub>3</sub>OH was mixed at 500rpm in a 5L Ecoclave pressure reactor from Büchi. The reactor was pressurised with 3bar CO<sub>2</sub> and the reaction was carried out at 55°C. After 4 days the temperature was lowered to room temperature and the reactor depressurised. The product was dried at 75°C in a vacuum oven for 3 days and then calcined at 250°C for 6 hours. Calcination was performed  
15 in order to assure decomposition of the organic intermediates formed in the reaction carried out in the pressure reactor. Upon this decomposition, magnesium carbonate is formed.

*Drug loading Procedure for Example 28*

- Ibuprofen was incorporated into the magnesium carbonate via a soaking method; 203.2 mg ibuprofen was dissolved in 50ml ethanol and then 642.7 mg of the magnesium carbonate was  
20 added to the solution. The mixture was placed on an orbital shaker at 100rpm at room temperature for 24h to allow for diffusion of ibuprofen into the magnesium carbonate. Subsequently the suspension was dried in an oven at 70°C to evaporate the solvent leaving a dry product containing 24wt% of Ibuprofen.

*Characterization for Example 28*

*X-ray powder diffraction (XRD)* analysis was performed with a D5000 diffractometer (40 kV, 40 mA, Siemens/Bruker) using Cu-K $\alpha$  radiation ( $\lambda=0.154$  nm). Samples were ground in a mortar and put on silicon sample holders with zero background prior to analysis.

- 5 *Fourier transform infrared spectroscopy (FTIR)* studies were performed, using a Bruker FTS 66v/s spectrometer with an Attenuated Total Reflectance (ATR) sample holder. All FTIR spectra were collected at a spectrum resolution of 4 cm $^{-1}$ , with 50 scans over the range from 4,000 to 500 cm $^{-1}$ . A background scan was acquired before scanning the samples.

- 10 *N<sub>2</sub> sorption analysis:* Gas sorption isotherms were obtained using an ASAP 2020 from Micromeritics, operated at 77 K. Prior to analysis the samples were degassed under vacuum at 338 K for 12 h prior to measurement. The specific surface area (SSA) was calculated using the multipoint Brunauer–Emmett–Teller (BET) method while the pore size distribution was calculated based on density functional theory (DFT) method using the model for N<sub>2</sub> at 77 K. These calculations were all performed using the ASAP 2020 (Micromeritics) software.

- 15 *Thermal gravimetric analysis (TGA)* was carried out on a Mettler Toledo, model TGA/SDTA851e, under an air flow in an inert alumina cup. The samples were heated from room temperature to 600°C with a heating rate of 3 K min $^{-1}$ .

- 20 *Differential scanning calorimetry (DSC)* was performed on a DSC Q2000 instrument from TA instruments using Exstar software. Samples of 3.5-5.5 mg were weighted into 5 mm Al pans and sealed. Samples were first cooled down to -35°C and then heated to 150 °C at a heating rate of 3K min $^{-1}$ . The instrument was calibrated for melting point and heat of fusion (T<sub>m</sub>[°C] and  $\Delta H_m$ [mJ mg $^{-1}$ ]) of Indium (156.6°C, 28.4 mJ mg $^{-1}$ ).

*Drug Release Measurement:* The release of ibuprofen was carried out in a USP-2 dissolution bath (Sotax AT7 Smart, Sotax AG, Switzerland) equipped with 1000mL vessels (37°C, 50 rpm). Samples with a total drug content of 17.5mg ibuprofen were placed in vessels containing 500mL phosphate buffer (pH=6.8). Measurements were made in triplicates on pure  
5 ibuprofen (IBU) crystals and ibuprofen loaded magnesium carbonate (MGCO3-IBU). Aliquots of 3 mL were withdrawn from each vessel at regular intervals for 125 min and the drug concentration in the liquid samples was analysed using UV/vis absorbance spectroscopy (1650PC, Shimadzu Corporation, Kyoto, Japan).

*Long-term Stability Test:* An MGCO3-IBU sample was stored in a desiccator at room  
10 temperature and 75% RH (obtained with a saturated aqueous mixture of water and NaCl) for 3 months. The sample was then analysed with XRD and DSC in order to investigate if a humid atmosphere induces crystallisation of the incorporated ibuprofen. Magnesium carbonate without ibuprofen was also stored under the same conditions to examine if the humidity affects the carrier material.

#### 15 *Results for Example 28*

After calcination, the Magnesium carbonate was in the form of white millimetre-sized particles. The peaks in the obtained XRD pattern correspond to unreacted MgO in the product while the lack of other peaks revealed that the magnesium carbonate component in the material is amorphous. The magnesium carbonate component of the material was evident  
20 from the FTIR spectra of the material, where absorption bands at  $\sim 850\text{ cm}^{-1}$ ,  $\sim 1100\text{ cm}^{-1}$  and  $\sim 1400\text{ cm}^{-1}$  stem from the carbonate group. The pore volume and mean pore size of the magnesium carbonate, as obtained from analysis of nitrogen sorption isotherms, are given in table 3 below.

**Table 3.** Results of material characterizations before and after ibuprofen loading as obtained from N<sub>2</sub> sorption experiments. The BET surface area was obtained as in above examples.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>pore</sub> (cm <sup>3</sup> /g)	D <sub>BJH</sub> (nm)
Magnesium carbonate	349	0.833	6.9
MGCO <sub>3</sub> -IBU	245	0.394	4.9

The pore size distribution obtained from the N<sub>2</sub> sorption analysis is given in Figure 34

- 5 After loading the magnesium carbonate with ibuprofen, TGA was carried out to investigate the drug loading degree in the carrier. From these it was evident that the free ibuprofen decomposed at about 200°C while the magnesium carbonate in the calcined material before drug loading decomposed into MgO and CO<sub>2</sub> at about 370°C. For the MGCO<sub>3</sub>-IBU sample two distinct weight loss regions were observed, the first related to the decomposition of
- 10 ibuprofen and the other related to the decomposition of the magnesium carbonate. The decomposition temperature of the incorporated ibuprofen was shifted 140°C to about 340°C compared to the free substance. The onset of decomposition for the magnesium carbonate was also shifted towards higher temperatures in the MGCO<sub>3</sub>-IBU sample, from about 320°C to 350°C compared to the calcined and unloaded material. From the TGA data it can be
- 15 calculated that the drug loading degree of ibuprofen in MGCO<sub>3</sub>-IBU is 24 wt% which corresponds to the magnesium carbonate/ibuprofen weight ratio in the preparation of the sample.

FTIR for MGCO<sub>3</sub>-IBU further confirmed successful incorporation of ibuprofen in the magnesium carbonate. In the absorbance spectra for the MGCO<sub>3</sub>-IBU, no new absorbance

20 bands compared to the free ibuprofen and the empty magnesium carbonate could be observed. This indicated that the adsorption of the ibuprofen in the pores of the magnesium carbonate was of physical character.

From the N<sub>2</sub> sorption data it can be seen that the mean pore diameter in the MGCO<sub>3</sub>-IBU sample is reduced with 2 nm compared to the empty magnesium carbonate and that the pore volume is reduced by about 50 %. The shift toward smaller pores related to narrowing of the pores in the empty magnesium carbonate when the material is filled with ibuprofen is also  
5 seen in the pore size distribution in Figure 34.

The XRD pattern for MGCO<sub>3</sub>-IBU lacks peaks corresponding to crystalline ibuprofen indicating a lack of crystallinity of the incorporated drug. The only peaks visible in the MGCO<sub>3</sub>-IBU XRD pattern stem from the MgO in the material. The lack of crystallinity of the ibuprofen in the MGCO<sub>3</sub>-IBU sample was further evident from the DSC curves. The  
10 endothermic event observed in these curves at 78°C for the free, crystalline ibuprofen corresponds to melting of the crystalline structure. The complete lack of an endothermic event at the same temperature for the MGCO<sub>3</sub>-IBU sample confirmed that the incorporated ibuprofen was not present in a crystalline state inside the pores. No peaks corresponding to any endo- or exothermic events could be detected in the DSC scan between -35°C to 150°C  
15 for the MGCO<sub>3</sub>-IBU sample. The XRD and DSC data shows that the the magnesium carbonate according to the invention suppresses crystallisation of the incorporated ibuprofen.

The dissolution profile of free ibuprofen and ibuprofen formulated with the magnesium carbonate can be seen in figure 35. The dissolution rate of the amorphous ibuprofen formulated with the magnesium carbonate according to the present invention is more rapid  
20 compared to the free substance. The dissolution rate for the amorphous ibuprofen is about three times faster during the first 5 minutes compared to the free substance and about 50% of the ibuprofen is dissolved and released from the carrier within 12 minutes while it takes about 30 minutes for the free substance to dissolve to the same level. The apparent solubility of the amorphous ibuprofen formulated with the magnesium carbonate according to the present  
25 invention is higher compared to the free substance.

In the stability test, no signs of crystallisation of the ibuprofen formulated with the magnesium carbonate could be detected with XRD and DSC after that the sample had been stored at 75%RH for three months at room temperature. Neither could any signs of crystallisation of the amorphous magnesium carbonate component in the formulation be detected when exposed to the humid atmosphere.

As appreciated by the skilled person the drug Ibuprofene should be considered as a non-limiting example of the use of the magnesium carbonate according to the present invention as a pharmaceutical or cosmetical excipient in combination with an active substance. In the case that the active substance is amorphous, crystallisation of the substance may be completely or partly suppressed by the magnesium carbonate leading to faster dissolution rate and/or increased solubility of the substance. The magnesium carbonate of the present invention is not only expected to act as a solubility enhancer when used as an excipient but also as, e.g., a pH modifier, tablet and capsule diluent, adsorbent, anti-caking agent and free-flowing agent.

#### EXAMPLE 29

The magnesium carbonate material was prepared as in as in the specific example described above with the alteration that the first drying time was reduced from 3 to 2 days. After 3 months of storage at 70 °C the material was dried/calcined using a temperature of 300 °C. The water sorption capacity of the calcined amorphous magnesium carbonate according to the invention was determined in the same way as described in example 1 with references to Fig. 5. The result for the calcined material is illustrated in Fig. 36. The measurements shows that the amorphous magnesium carbonate according to the present invention after calcination adsorbs more than 0.6 mmol water /g material and even more than 0.7 mmol water /g material at an RH of 3% at room temperature. At an RH of 10% at room temperature the calcined amorphous magnesium carbonate adsorbs more than 1.5 mmol water /g material and even



more than 1.7 mmol water /g material. At an RH of 90% at room temperature the calcined amorphous magnesium carbonate adsorbs more than 15 mmol water /g material and even more than 20 mmol water /g material.

Although the present invention has been described in connection with preferred embodiments  
5 thereof, it will be appreciated by those skilled in the art that additions, deletions, modifications, and substitutions not specifically described may be made without departure from the spirit and scope of the invention as defined in the appended claims.

## CLAIMS

What is claimed is:

- 5 1. A magnesium carbonate, wherein the magnesium carbonate is X-ray amorphous, and wherein the magnesium carbonate is characterized by a cumulative pore volume of pores with a diameter smaller than 10 nm of at least  $0.018 \text{ cm}^3/\text{g}$ , preferably at least  $0.4 \text{ cm}^3/\text{g}$ , more preferably at least  $0.8 \text{ cm}^3/\text{g}$ .
- 10 2. The magnesium carbonate of claim 1, wherein the magnesium carbonate is characterized by a BET specific surface area obtained from  $\text{N}_2$  sorption isotherms of between  $60 \text{ m}^2/\text{g}$  and  $1500 \text{ m}^2/\text{g}$ , preferably between  $100 \text{ m}^2/\text{g}$  and  $1500 \text{ m}^2/\text{g}$ , more preferably between  $240 \text{ m}^2/\text{g}$  and  $1500 \text{ m}^2/\text{g}$  and most preferably between  $600 \text{ m}^2/\text{g}$  and  $1500 \text{ m}^2/\text{g}$ .
- 15 3. The magnesium carbonate of claim 2, wherein the cumulative pore volume of pores with a diameter smaller than 10 nm is between  $0.018 \text{ cm}^3/\text{g}$  and  $3.0 \text{ cm}^3/\text{g}$ , preferably between  $0.018 \text{ cm}^3/\text{g}$  and  $1.5 \text{ cm}^3/\text{g}$ .
4. The magnesium carbonate of claim 1, wherein the magnesium carbonate is  
20 characterized by adsorbing more than  $0.3 \text{ mmol water/g}$  material at an RH of 3% at room temperature, preferably adsorbing more than  $0.6 \text{ mmol water/g}$  material at an RH of 10% at room temperature, more preferably adsorbing more than  $14 \text{ mmol water/g}$  material at an RH of 90% at room temperature.
- 25 5. A desiccant comprising the magnesium carbonate as in any of the proceeding claims.

6. A powder or a pellet or a film comprising the magnesium carbonate as in any of the proceeding claims.

5 7. An additive to a food, a chemical, a cosmetic or a pharmaceutical comprising the magnesium carbonate as in any of the proceeding claims.

8. An excipient in a cosmetic or a pharmaceutical comprising the magnesium carbonate as in any of the proceeding claims.

10

9. A method to produce magnesium carbonate, the method comprising:  
reacting an inorganic magnesium compound with alcohol in a CO<sub>2</sub> atmosphere,  
wherein the pressure is above atmospheric pressure.

15 10. The method of claim 9, wherein the temperature is between 40 °C to a boiling temperature of the alcohol.

11. The method of claim 9, wherein the pressure is 1 to 3 bar above atmospheric pressure.

20 12. The method of claim 9, wherein the produced magnesium carbonate is X-ray amorphous, and

wherein the produced magnesium carbonate is characterized by a cumulative pore volume of pores with a diameter smaller than 10 nm of between 0.018 cm<sup>3</sup>/g and 3.0 cm<sup>3</sup>/g, preferably between 0.018 cm<sup>3</sup>/g and 1.5 cm<sup>3</sup>/g.

25

13. The method of claim 12, wherein the magnesium carbonate is characterized by a BET specific surface area obtained from N<sub>2</sub> sorption isotherms of between 60 m<sup>2</sup>/g and 1500 m<sup>2</sup>/g, preferably between 100 m<sup>2</sup>/g and 1500 m<sup>2</sup>/g, more preferably between 240 m<sup>2</sup>/g and 1500 m<sup>2</sup>/g and most preferably between 600 m<sup>2</sup>/g and 1500 m<sup>2</sup>/g.

5

14. The method of claim 9, wherein the inorganic magnesium compound is MgO.

15. A method to produce magnesium carbonate, the method comprising the steps of:

mixing a Mg-containing precursor and an alcohol-containing liquid in a reactor,

10 to form at least one Mg-based intermediary that can interact with CO<sub>2</sub>;

forming a carbonated intermediate product by reacting the at least one Mg-based intermediary with CO<sub>2</sub>, wherein the carbonated intermediate is a liquid or a gel; and

transforming the liquid or gel carbonated intermediate product into magnesium carbonate by drying,

15 wherein the magnesium carbonate is X-ray amorphous, and

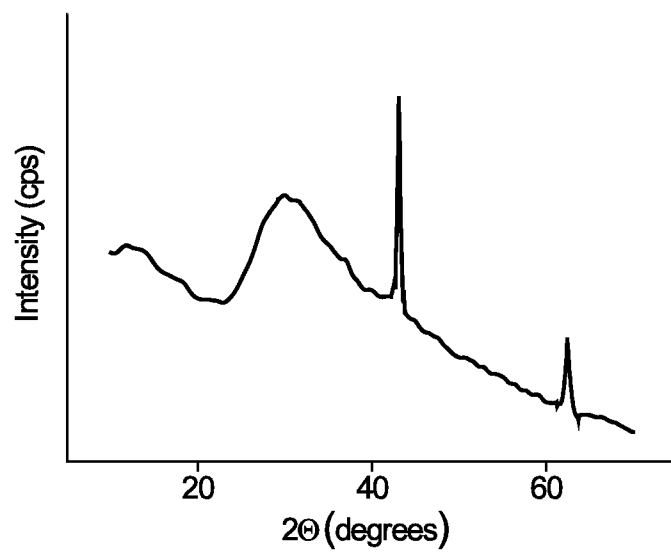
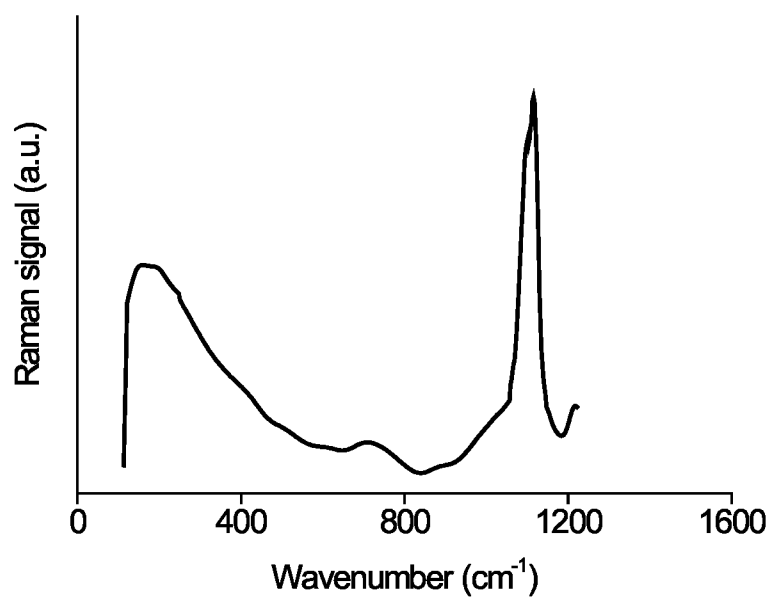
wherein the magnesium carbonate is characterized by a cumulative pore volume of pores with a diameter smaller than 10 nm of at least 0.018 cm<sup>3</sup>/g, preferably at least 0.4 cm<sup>3</sup>/g, more preferably at least 0.8 cm<sup>3</sup>/g.

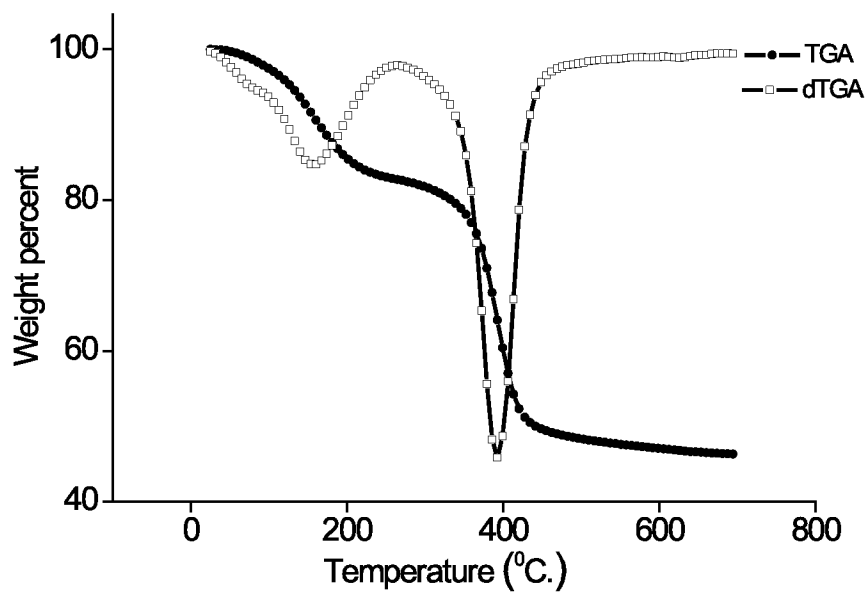
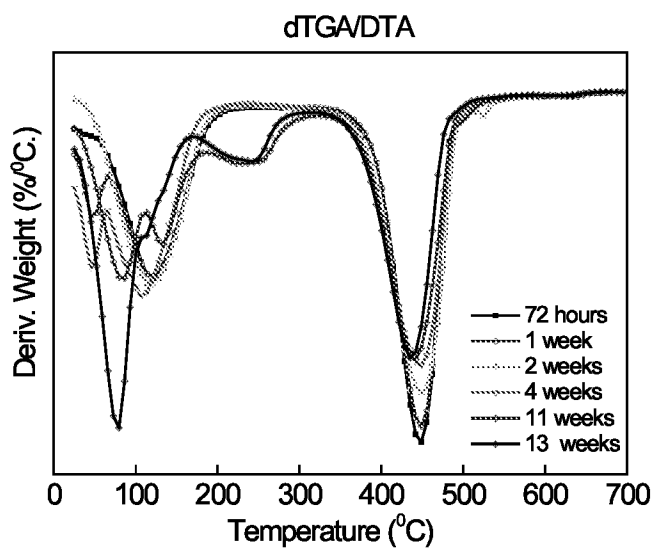
20 16. The method of claim 15, wherein mixing is performed at a temperature between 40°C and a boiling temperature of the alcohol-containing liquid.

17. The method of claim 15, wherein forming the carbonated intermediate product is performed at a temperature below 50°C and a pressure above atmospheric pressure.

25

18. The method of claim 15, wherein the pressure is less than 5 bar above atmospheric pressure.
19. The method of claim 15, wherein drying is performed at a temperature between 60 °C  
5 and 300 °C.
20. The method of claim 15, wherein the cumulative pore volume of pores with a diameter smaller than 10 nm is between 0.018 cm<sup>3</sup>/g and 3.0 cm<sup>3</sup>/g, preferably between 0.018 cm<sup>3</sup>/g and 1.5 cm<sup>3</sup>/g, and  
10 wherein the magnesium carbonate is characterized by a BET specific surface area obtained from N<sub>2</sub> sorption isotherms of between 60 m<sup>2</sup>/g and 1500 m<sup>2</sup>/g, preferably between 100 m<sup>2</sup>/g and 1500 m<sup>2</sup>/g, more preferably between 240 m<sup>2</sup>/g and 1500 m<sup>2</sup>/g and most preferably between 600 m<sup>2</sup>/g and 1500 m<sup>2</sup>/g.
- 15 21. A method of controlling moisture content in a volume of a material, comprising exposing the volume to the magnesium carbonate as in any of the claims 1 to 4.

*Figure 1.**Figure 2.*

*Figure 3.**Figure 4.*

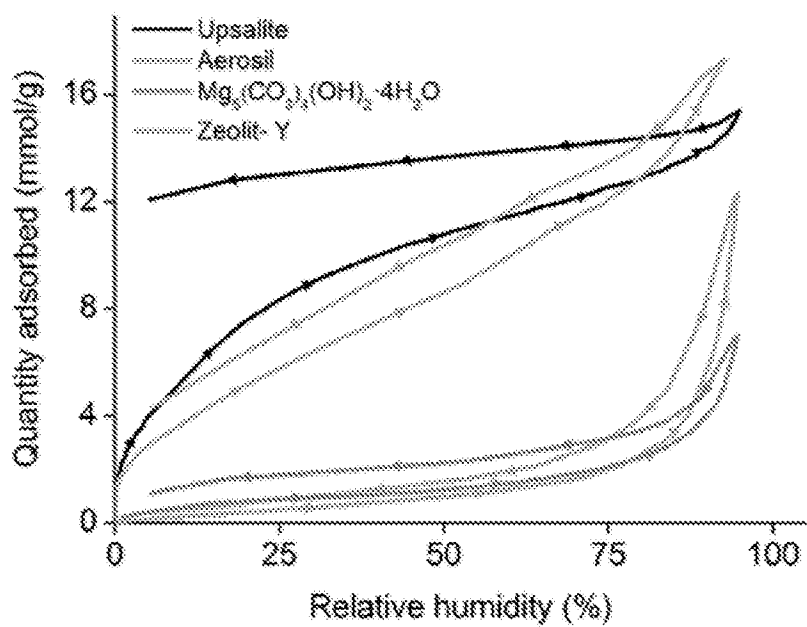


Figure 5.

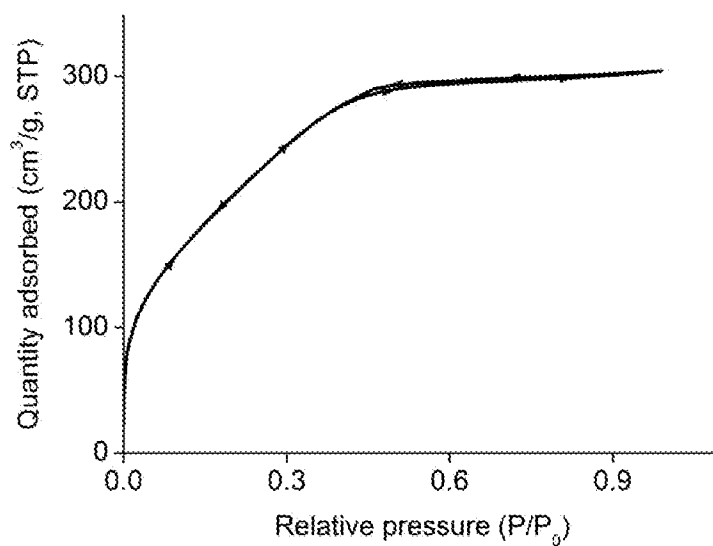
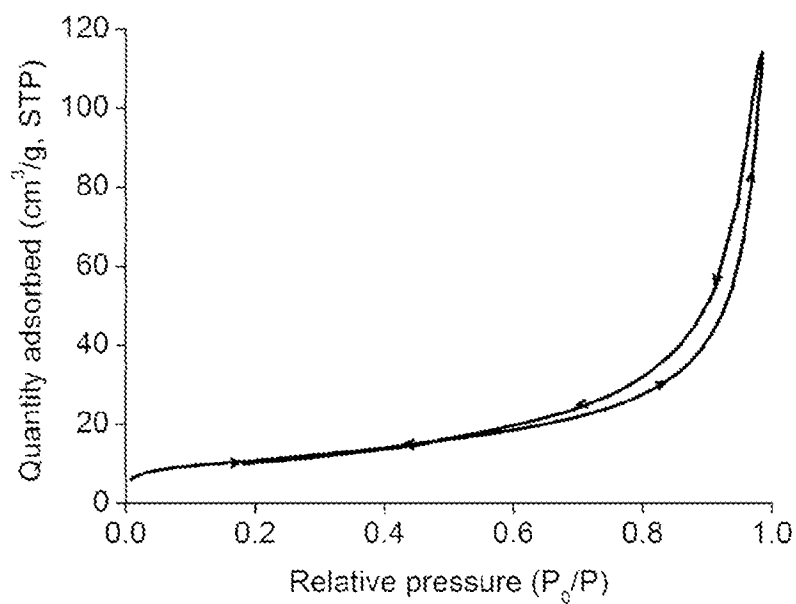
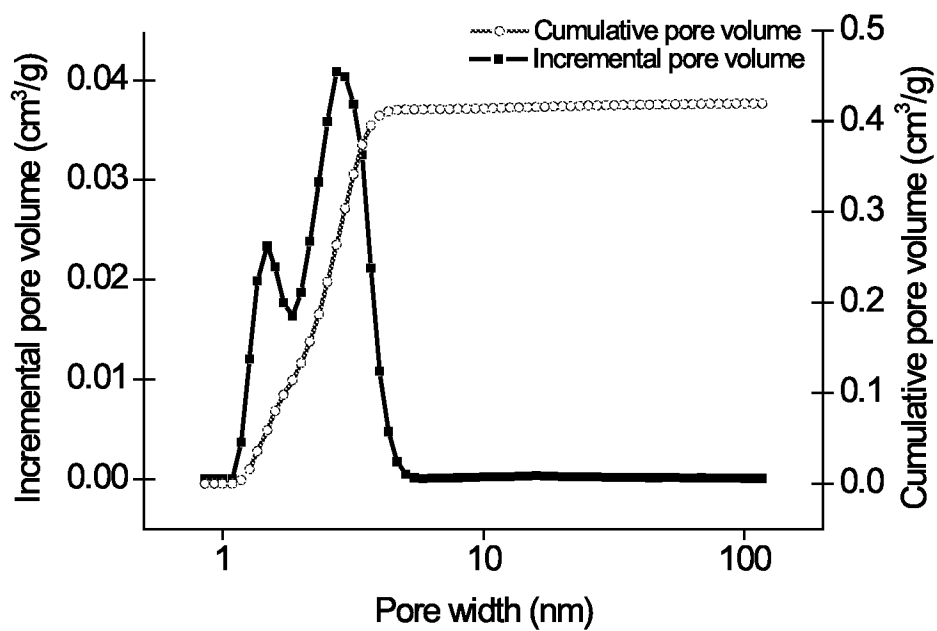
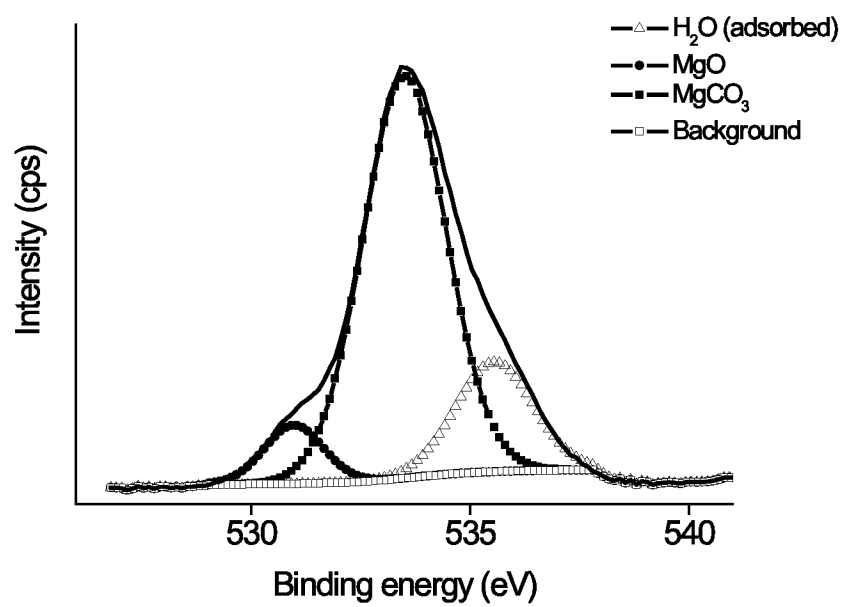
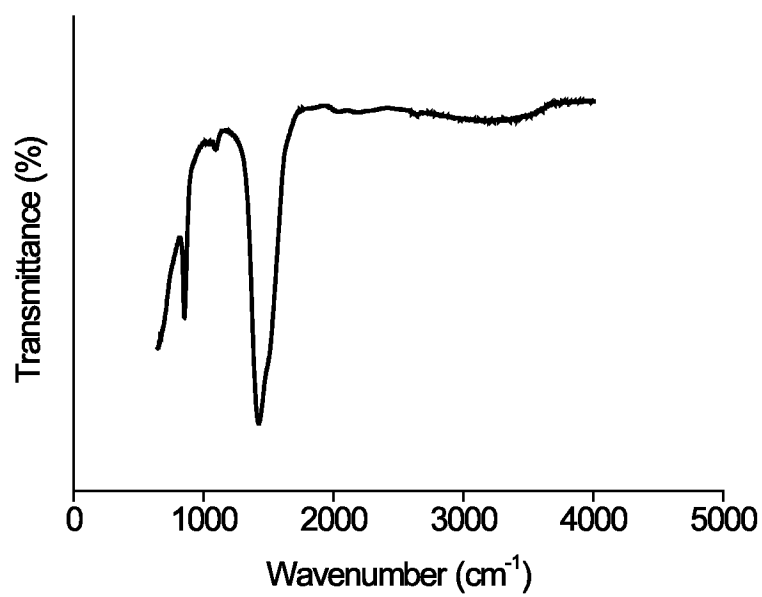
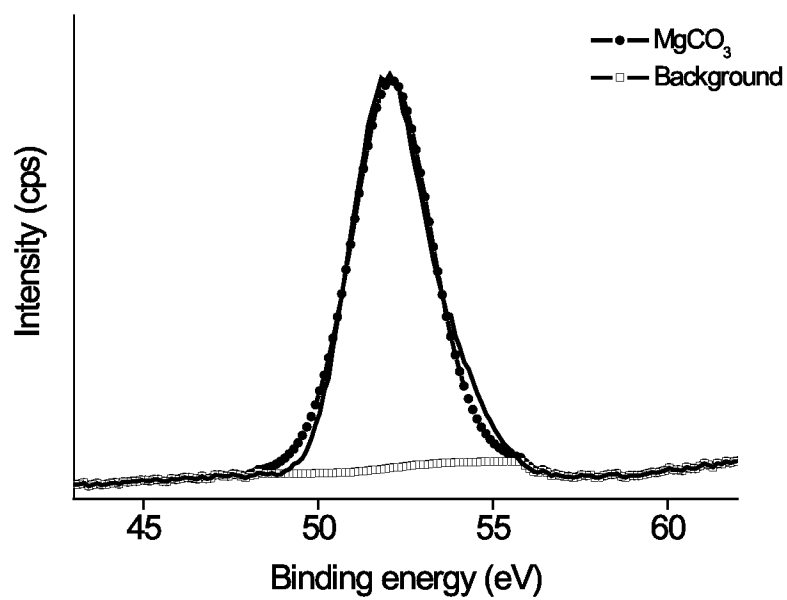


Figure 6.

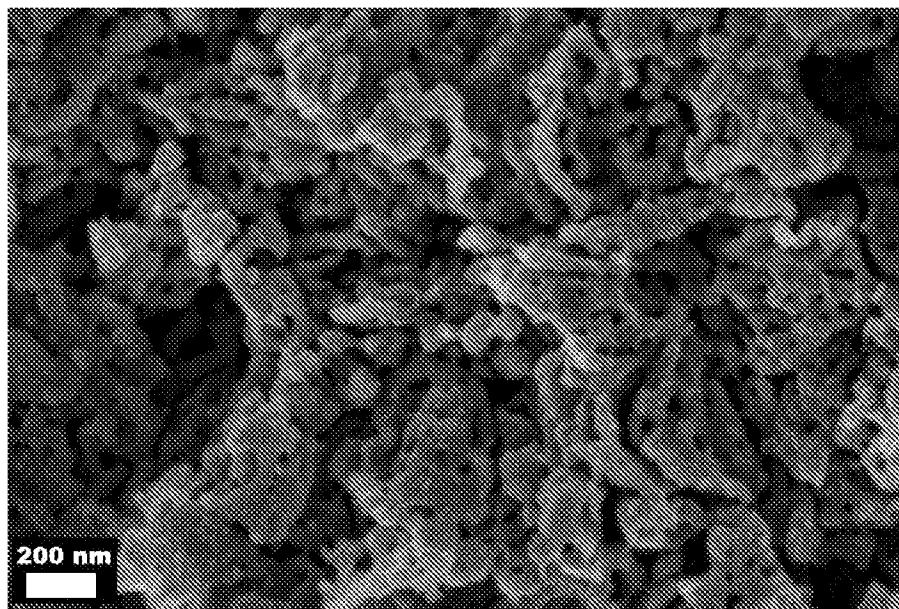


*Figure 7.**Figure 8.*

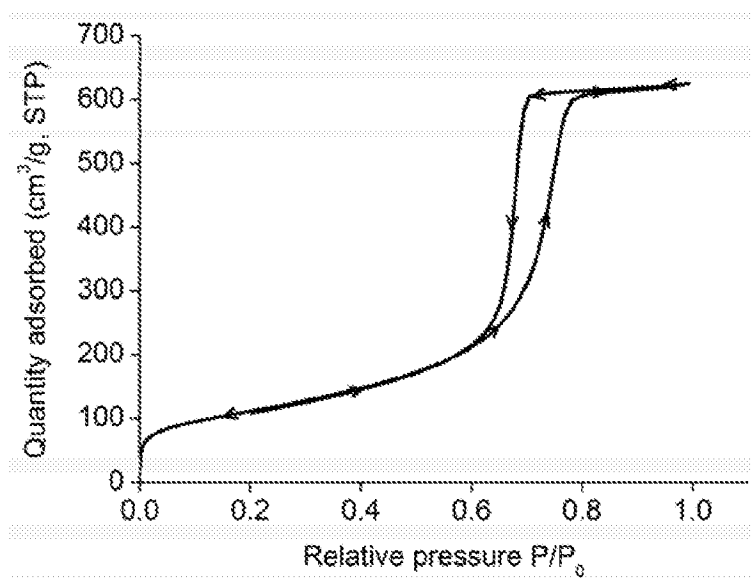
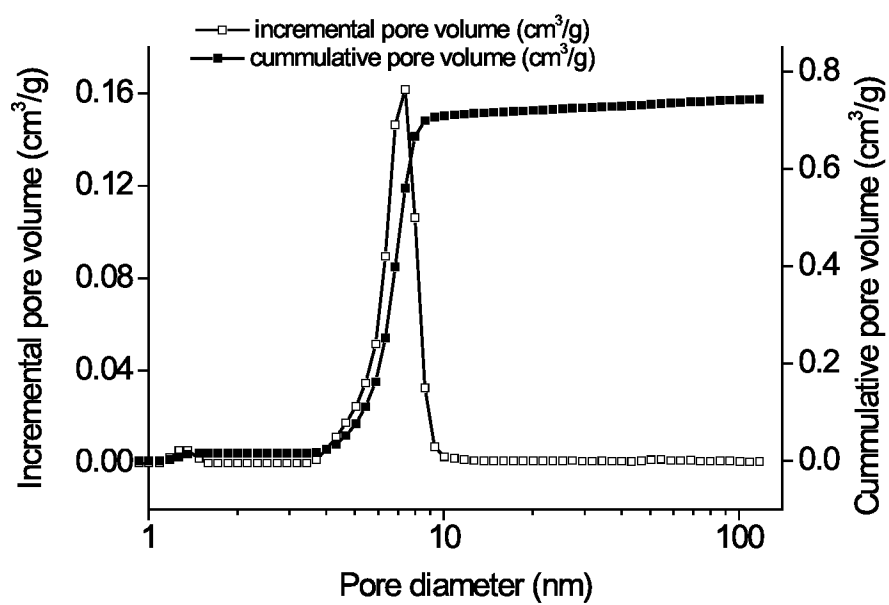
*Figure 9.**Figure 10.*

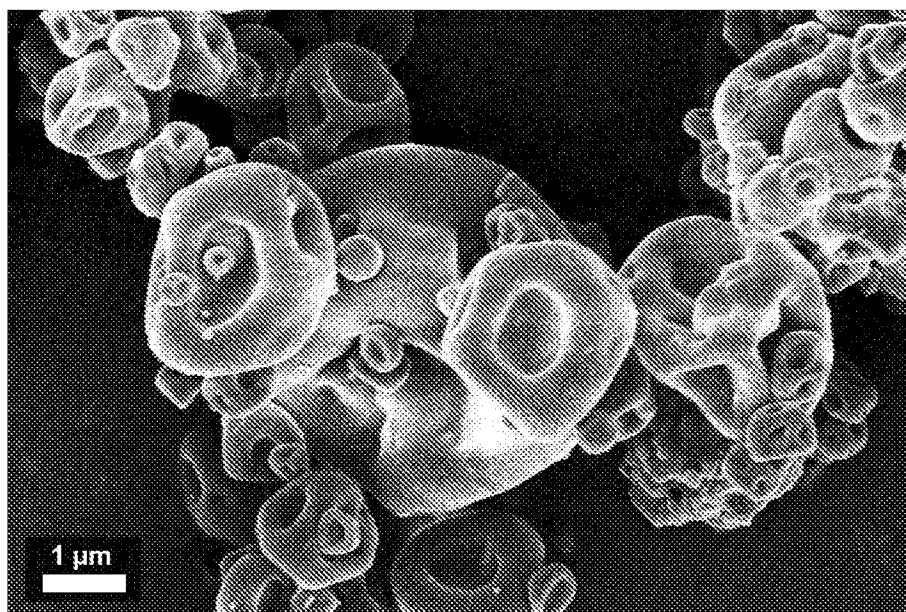


*Figure 11.*

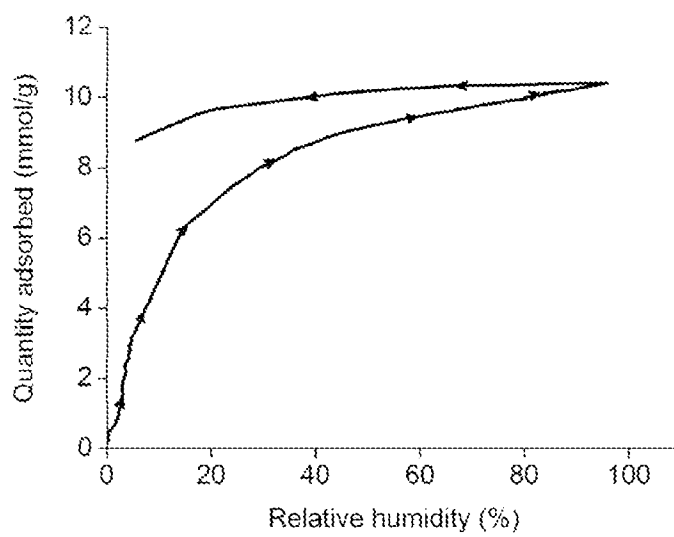


*Figure 12.*

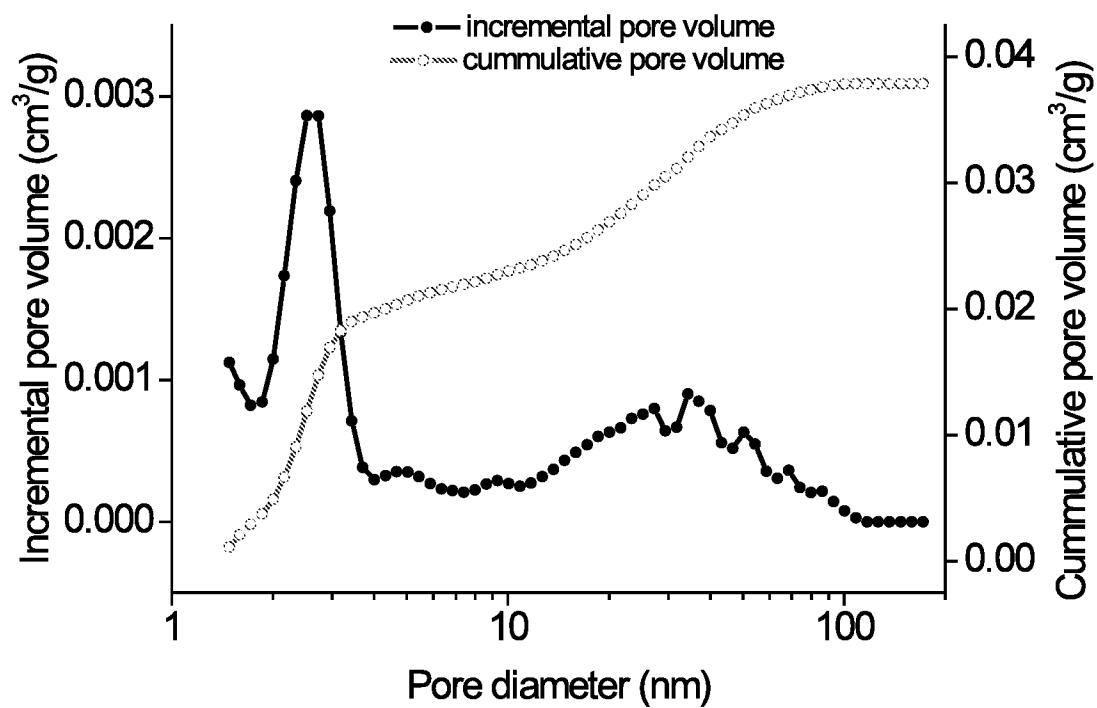
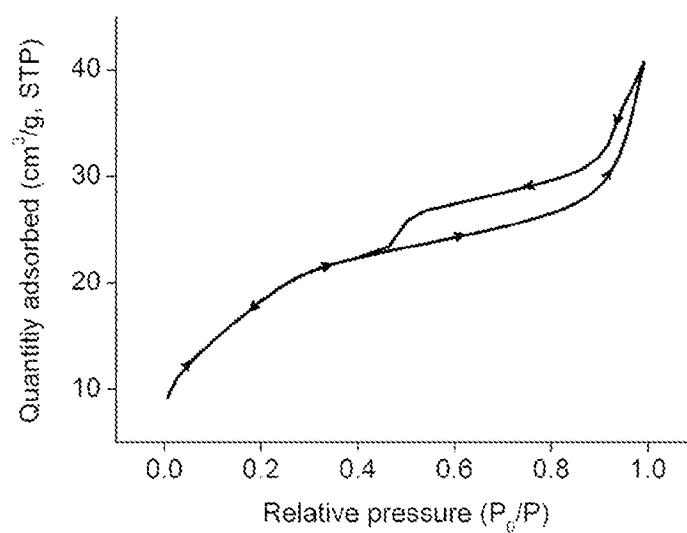
*Figure 13.**Figure 14.*

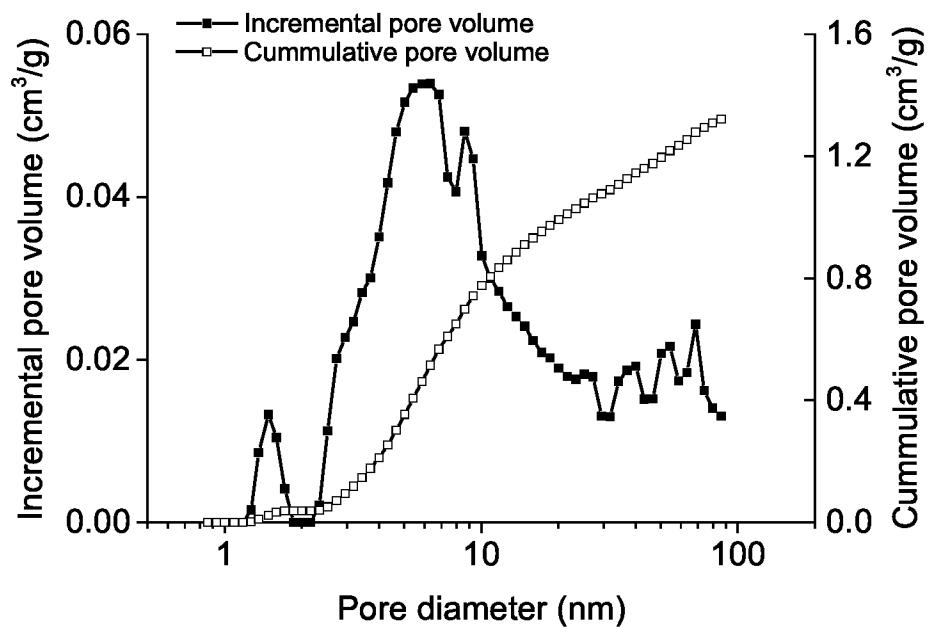
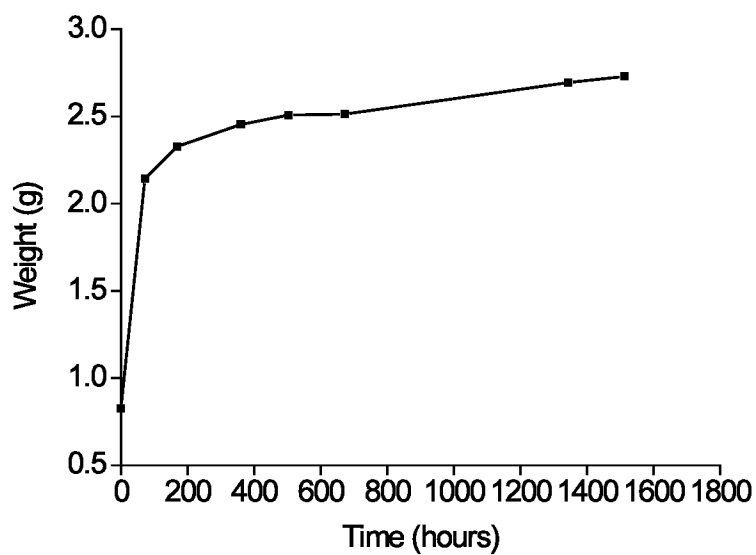


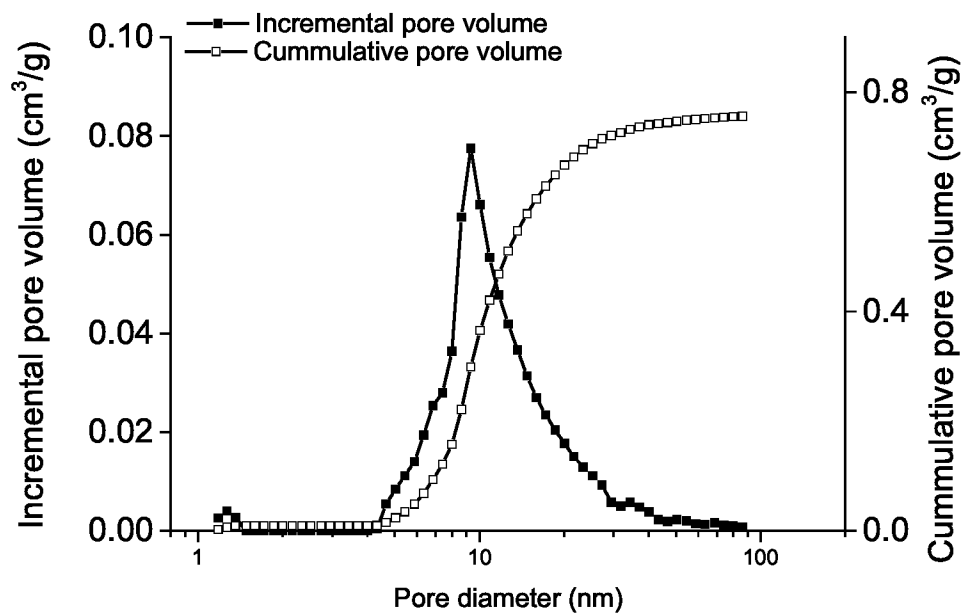
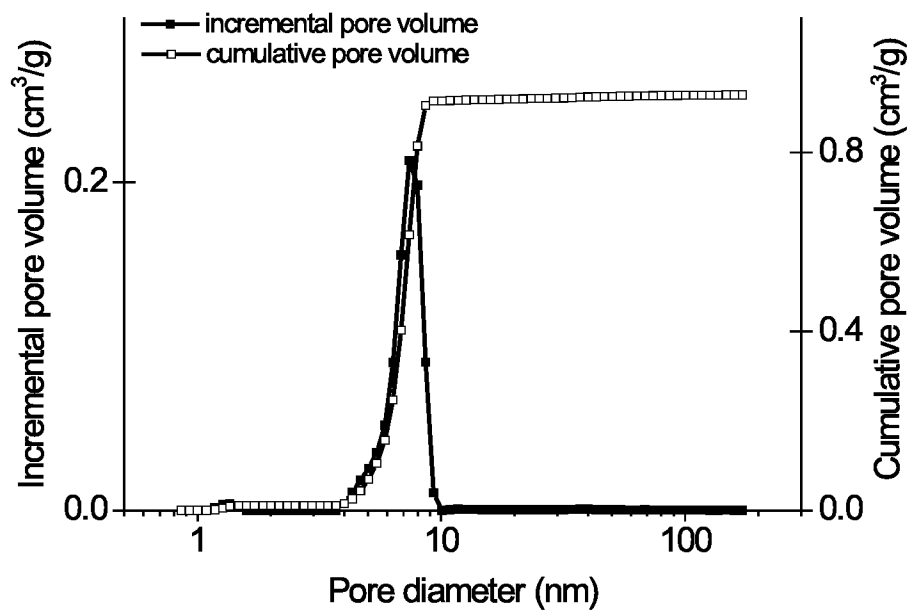
*Figure 15.*



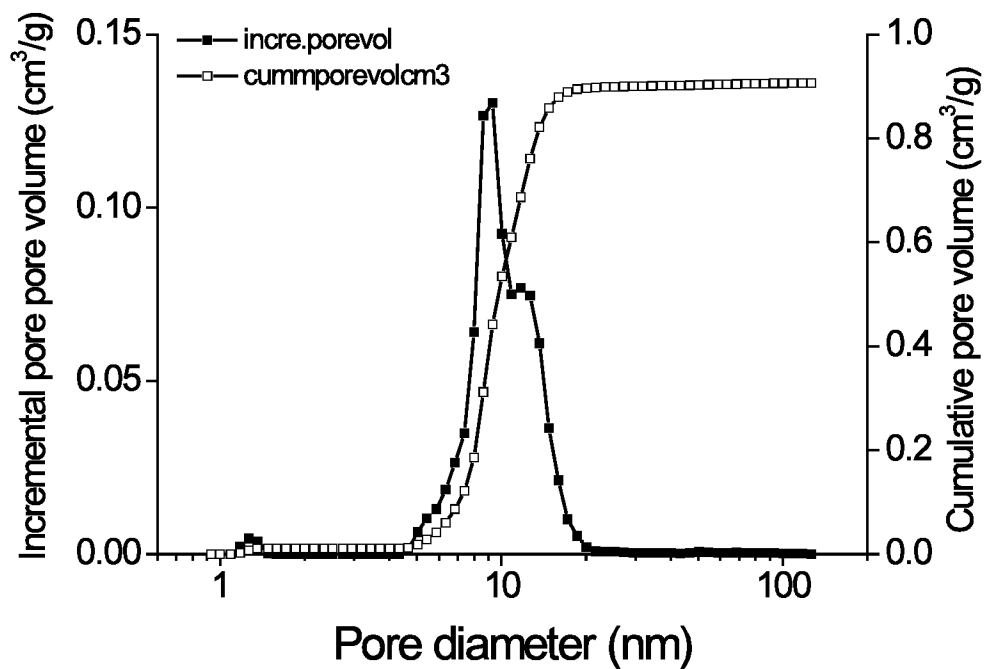
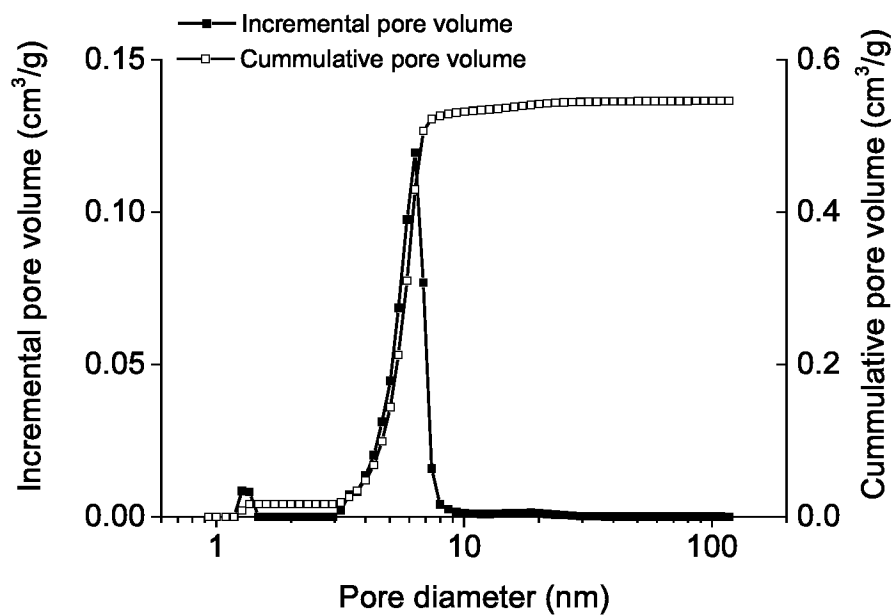
*Figure 16.*

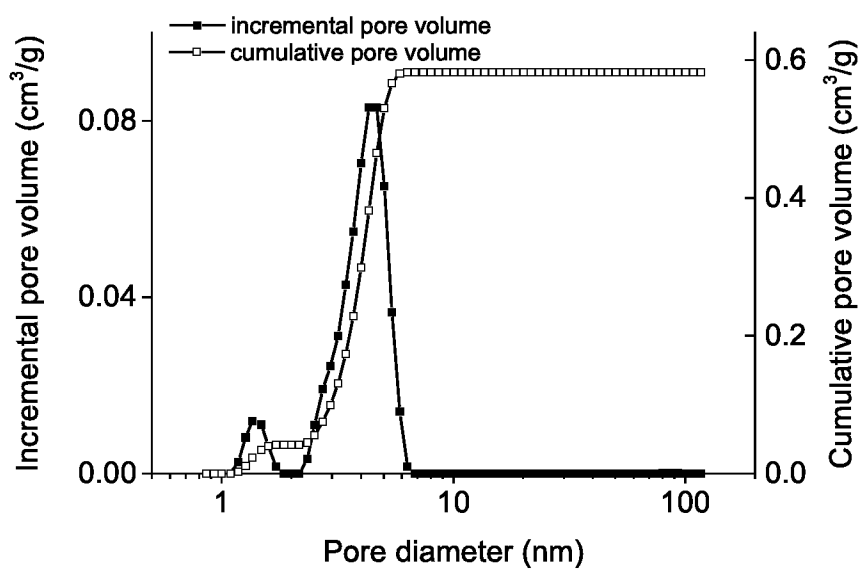
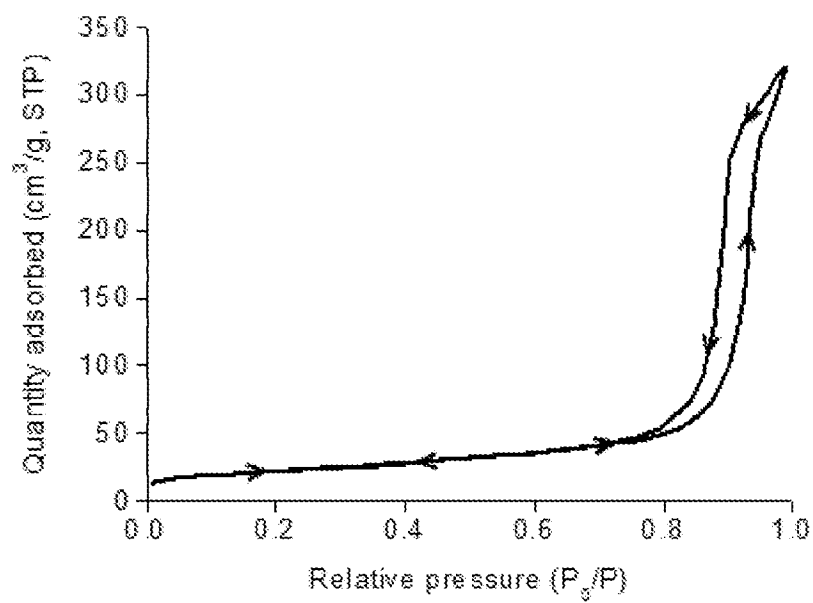
*Figure 17.**Figure 18.*

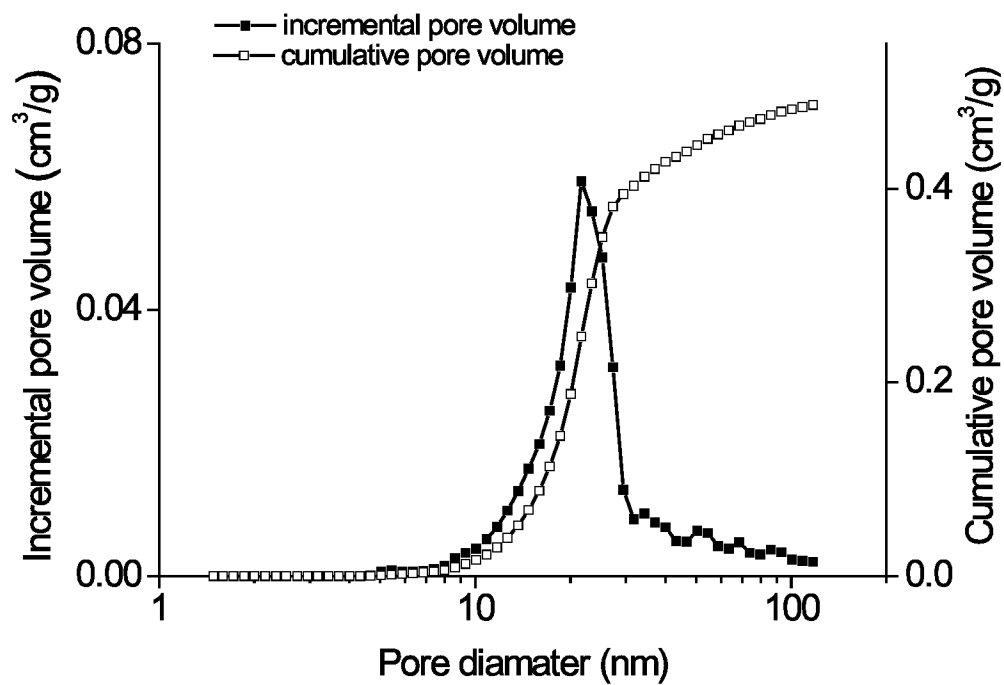
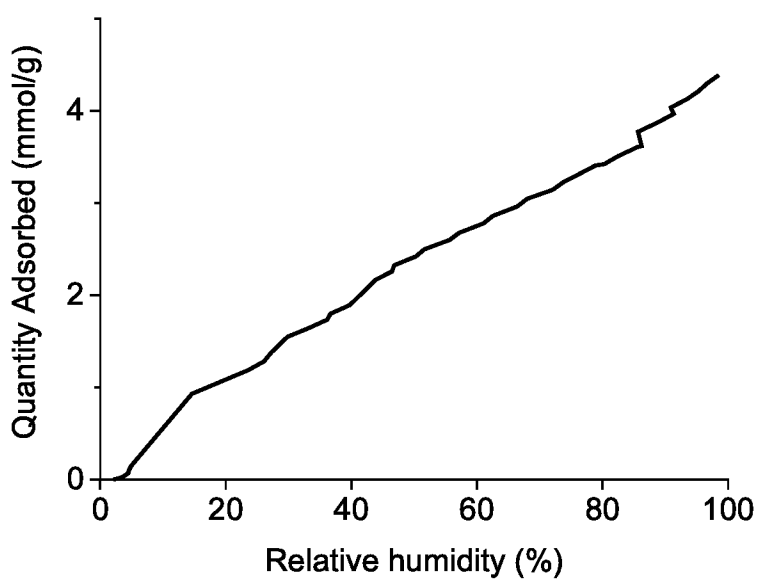
*Figure 19.**Figure 20.*

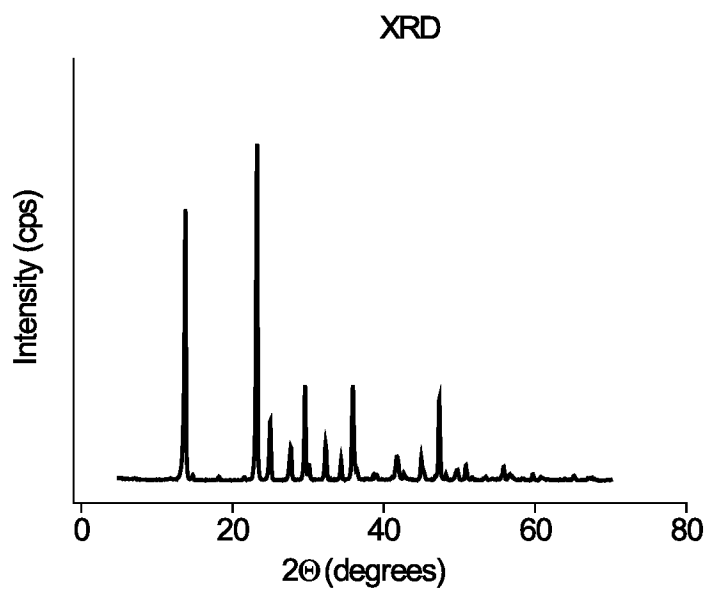
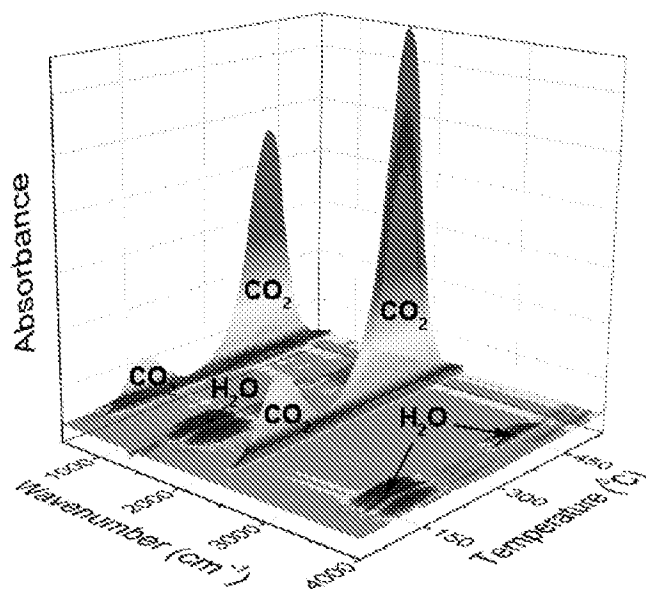
*Figure 21.**Figure 22.*

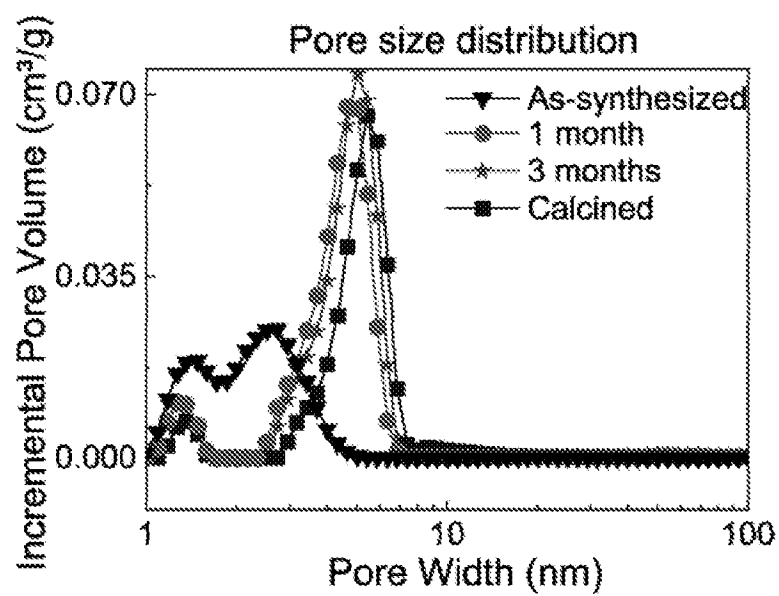
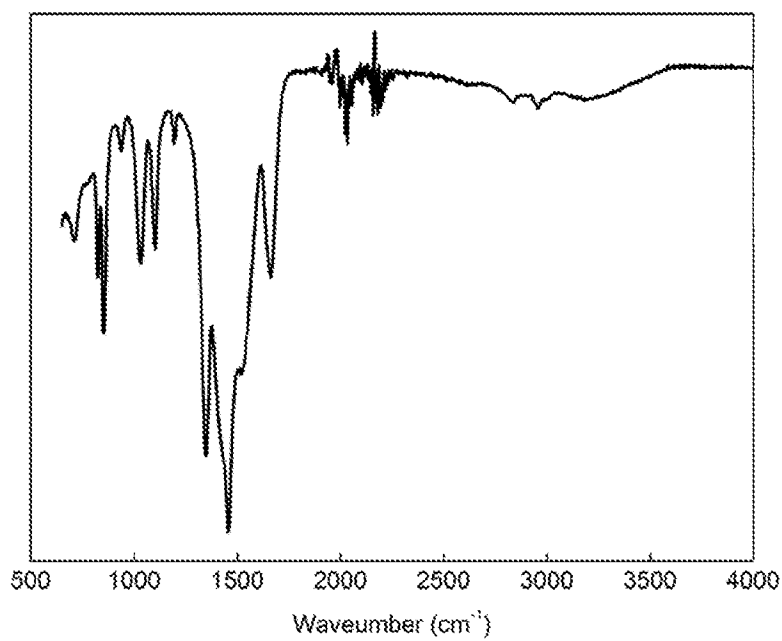


*Figure 23.**Figure 24.*

*Figure 25.**Figure 26.*

*Figure 27.**Figure 28.*

*Figure 29.**Figure 30.*

*Figure 31.**Figure 32.*

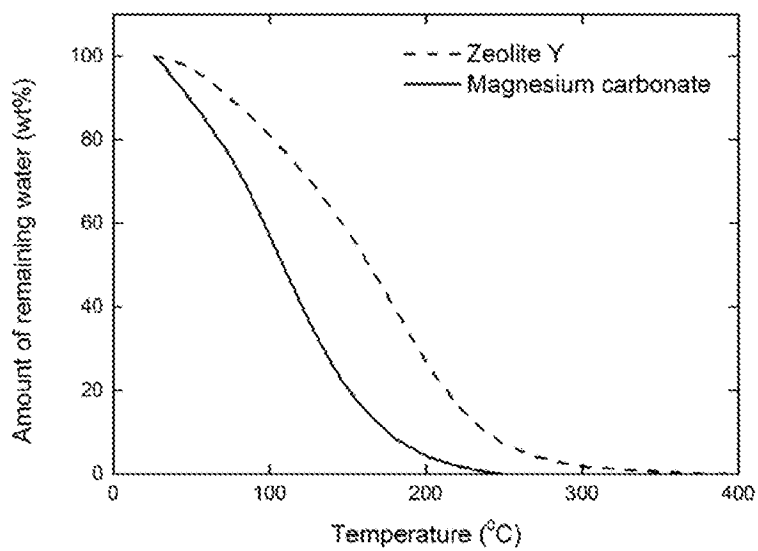


Figure 33.

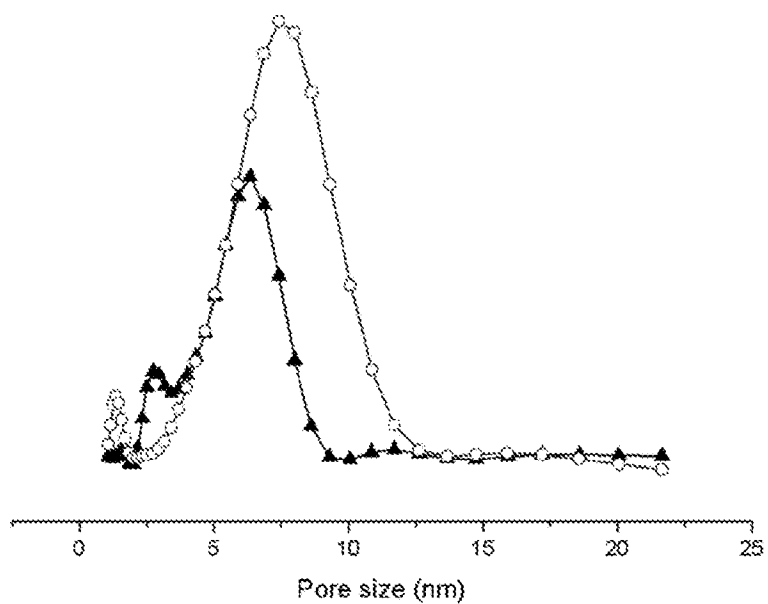


Figure 34.

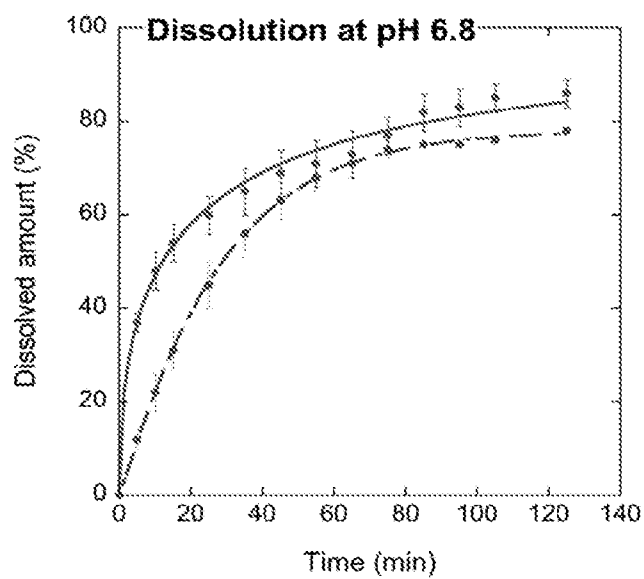


Figure 35.

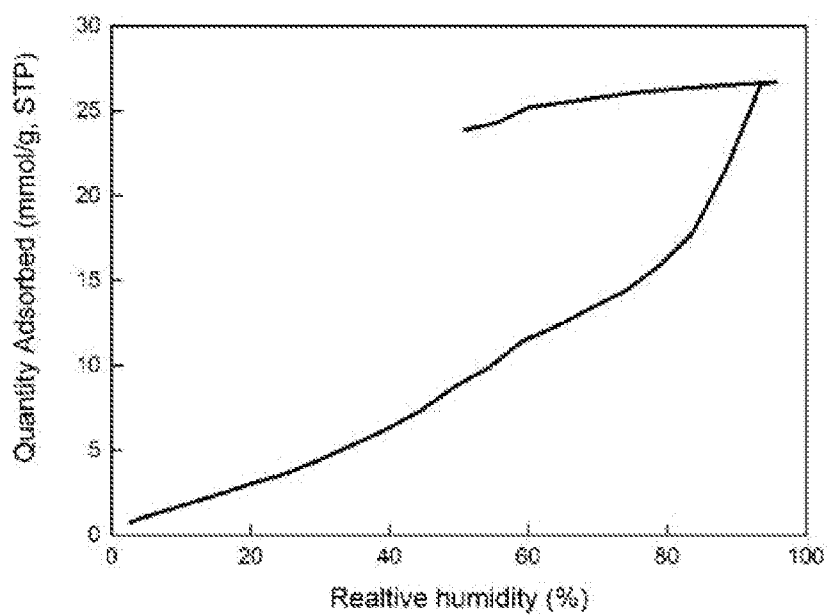


Figure 36.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2013/060647

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C01F5/24 A61K8/19 B01J20/04 C01B31/24  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01F A61K B01J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2004 203700 A (NITTETSU MINING CO LTD) 22 July 2004 (2004-07-22)	1-8,21
A	paragraphs [0014], [0016], [0021], [0047]	9-20
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X	EP 2 206 681 A2 (KOREA INST SCI & TECH [KR]) 14 July 2010 (2010-07-14)	9,10,15, 17,20
A	paragraphs [0015], [0016], [0018], [0019], [0022] - [0025]; example 3	1-8, 11-14, 16,18, 19,21
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A	US 5 240 692 A (MORIFUJI TETSUHIKO [JP]) 31 August 1993 (1993-08-31) column 2, lines 3-40 column 4, lines 14-38	1-21
	-----	
	-/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

2 May 2014

Date of mailing of the international search report

15/05/2014

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# INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2013/060647

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>C. NEUBERG &amp; B. REWALD: "Ueber kolloide und gelatinöse Verbindungen der Erdaalkalien",  ZEITSCHRIFT FÜR CHEMIE UND INDUSTRIE DER KOLLOIDE,  vol. 2, no. 12, June 1908 (1908-06), pages 354-357, XP002723900,  page 356</p> <p style="text-align: center;">-----</p>	1-21

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2013/060647

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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			JP 2004203700 A	22-07-2004
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			US 2010178227 A1	15-07-2010
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			US 5240692 A	31-08-1993
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