Title: FERTILIZER COMPOSITION AND PROCESS TO PREPARE SAID FERTILIZER COMPOSITION

Abstract: The present invention provides a fertilizer composition comprising spent phosphorus-comprising molecular sieve catalyst obtained from a process for converting methanol to olefins. In a further aspect the invention also relates to a process for preparing such fertilizer composition and a method to introduce phosphorus to a substrate to promote plant growth.
FERTILIZER COMPOSITION AND PROCESS TO PREPARE SAID

FERTILIZER COMPOSITION

Field of the invention

The invention relates to a fertilizer composition, a process to prepare said fertilizer composition and a method to introduce phosphorus to a substrate to promote plant growth.

Background of the invention

In recent years there has been an increasing demand for phosphorus containing fertilizers. The demand for phosphorus for fertilizer, but also for a multitude of other purposes, however has lead to increasing concerns that there may be a shortage of phosphorus in the future.

In order to make efficient use of the available phosphorus has been considered to reuse or recycle phosphorus, originally used for purposes other than fertilizer. Such recycled phosphorus may serve as an alternative to fresh phosphorus when preparing phosphorus containing fertilizers.

Phosphorus is widely used as a catalyst or catalyst-component in the chemical and petrochemical industry. Due to the limited lifespan of these catalysts, large quantities of spent phosphorus catalyst are annually disposed in landfills. There has been some interest in using spent phosphorus catalysts as fertilizer as described by Van der Merwe (W. Ven der Merwe, Environ. Sci. Technol., Vol 44, Issue 5, 2010, p1806-1812). Van der Merwe describes the use of solid phosphoric acid (SPA) catalyst as fertilizer. Although, Van der Merwe shows that the phosphorus in the SPA may be suitably used as a source of phosphorus, chemical analysis of the SPA catalyst and the fertilizers
produced with the SPA catalyst show that these fertilizers may comprises significant amounts of heavy metals such as Ni, V, Co, Cr, and Sr, which makes them less suitable for use in food crop fertilizers. One reason for the presence of these heavy metals may be the fact that the SPA catalyst are commonly used in hydrocarbon conversion processes that use crude oil or crude oil fractions as a feedstock. These feedstocks can contain significant amounts of heavy metals that are subsequently deposited on the catalyst during operation.

There is a need for fertilizers comprising phosphorus based on spent catalyst comprising less heavy metals.

Summary of the invention

It has new been found that spent phosphorus-comprising molecular sieve catalyst obtained from a methanol to olefins process can be used as or as part of a fertilizer.

Accordingly, the present invention provides a fertilizer composition comprising spent phosphorus-comprising molecular sieve catalyst obtained from a process for converting methanol to olefins.

Common MTO catalysts comprise molecular sieve compounds having phosphorus deposited on the molecular sieve structure or alternatively incorporated in the molecular sieve structure as framework phosphorus. This phosphor may advantageously be utilized as a nutrient in a fertilizer composition.

Typical SPA catalyzed oil conversion processes, but also well known processes such as for instance phosphorus-comprising molecular sieve catalyzed FCC processes, use feedstocks that are crude oil-fractions or crude oil-based and comprise significant amounts of V and Ni, in addition to numerous other heavy metals. These
metals are deposited on the catalyst making it unsuitable for use in fertilizer compositions. Contrary to SPA catalyzed oil conversion and FCC processes, methanol to olefin (MTO) processes use a methanol feedstock that does not comprise significant amounts, if any, of heavy metals.

In another aspect the invention provides for a process for preparing a fertilizer composition, comprising:

1. providing a phosphorus-comprising molecular sieve catalyst;
2. subjecting the catalyst to one or more methanol-to-olefin conversion and catalyst regeneration cycles;
3. withdrawing at least part of the catalyst as spent phosphorus-comprising molecular sieve catalyst;
4. formulating a fertilizer composition comprising the spent phosphorus-comprising molecular sieve catalyst.

In a further aspect, the invention provides a method to introduce phosphorus to a substrate to promote plant growth, comprising applying a fertilizer composition according to the invention to a substrate used to grow plants.

Detailed description of the invention

The present invention provides a fertilizer or fertilizer composition comprising spent phosphorus-comprising molecular sieve catalyst obtained from a process for converting methanol to olefins. A fertilizer is a compound or composition intended to introduce nutrients, such as phosphorus to a substrate to promote plant growth. Reference herein to a fertilizer is to a
fertilizer, a fertilizer composition or fertilizer formulation. The fertilizer may consist of or comprise spent phosphorus-comprising molecular sieve catalyst. Preferably the fertilizer composition comprises spent phosphorus-comprising molecular sieve catalyst, but also comprises other components that may aid the fertilizer function or improve the distribution or handling of the fertilizer. The fertilizer may be applied on top of a substrate, i.e. the soil or (artificial) plant growing medium or may be mixed or incorporated with the substrate. Alternatively, the fertilizer may be applied as a separate layer below a top substrate layer.

Phosphorus is known as one of the six macronutrients, i.e. nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and sulfur (S). Generally, a fertilizer composition will comprise one or more of these macronutrients. In the present invention, the fertilizer composition will comprise at least phosphorus, which phosphorus is at least partly provided in the form of a phosphorus-comprising molecular sieve catalyst obtained from a process for converting methanol to olefins.

The phosphorus-comprising molecular sieve is a molecular sieves having a molecular framework of one, preferably two or more corner-sharing [T04] tetrahedral units, more preferably, two or more [Si04], [Al04] and/or [P04] tetrahedral units. These silicon, aluminum and/or phosphorus based molecular sieves and metal containing silicon, aluminum and/or phosphorus based molecular sieves have been described in detail in numerous publications including for example, U.S. Pat. No. 4,567,029. In a preferred embodiment, the molecular sieves have 8-, 10- or 12-ring structures and an average pore size in the range of from about 3 Å to 15 Å.
Suitable molecular sieves are silicoaluminophosphates (SAPO), such as SAPO-17, -18, -34, -35, -44, but also SAPO-5, -8, -11, -20, -31, -36, -37, -40, -41, -42, -47 and -56; and aluminophosphates (AlPO). Another type of molecular sieve that may be used is a metal substituted (silico) aluminophosphates (MeAlPO), wherein the Me in MeAlPO refers to a substituted metal atom selected from the group consisting of K, Ca or Mg. As mentioned above, these metal are also considered as macronutrients and can suitably be included into the fertilizer in the form of a MeAlPO.

In addition to the above mentioned macronutrients, several other elements are regarded as micronutrients. These micronutrients include boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), and zinc (Zn). Although fertilizer compositions comprise much lower concentrations of these micronutrients in comparison to the before mentioned macronutrients it may be preferred that the fertilizer composition comprises MeAlPO molecular sieves, wherein the Me in MeAlPO refers to a substituted metal atom selected from the group consisting of B, Cu, Fe, Mn, Mo and Zn. As mentioned above, these metals are also considered as micronutrients and can suitably be included into the fertilizer in the form of a MeAlPO. Where the macronutrients are consumed in larger quantities and are present in plant tissue, i.e. in typical quantities from 0.15% to 6.0% on a dry matter basis, micronutrients are consumed in smaller quantities and are present in plant tissue on the order of parts per million (ppm), ranging from 0.15 to 400 ppm on a dry matter basis. Therefore, although where MeAlPO molecular sieves, wherein the Me in MeAlPO refers to a above mentioned micronutrient metal, may be present in
the fertilizer it will preferably be in low concentration, preferably below 0.1wt%, more preferably 0.05wt% metal based on the fertilizer composition. MeAlPO molecular sieves, wherein the Me in MeAlPO refers to a substituted metal atoms such as Co, Cr, Ga, Ge, Ni, V are not suitable for the purpose to the present invention. The substituted metals are regarded as toxic to the environment and therefore not suitable as fertilizers.

Other suitable molecular sieves are zeolites. Although, contrary to SAPO, A1PO and MeAlPO type molecular sieves, zeolites do not contain framework phosphorus, phosphorus is applied to the zeolites either by pre-treating the zeolites or intermediate or post-treating a zeolite-comprising catalyst formulation to introduce phosphorus. Suitable zeolites include those of the ZSM group, in particular of the MFI type, such as ZSM-5, the MTT type, such as ZSM-23, the TON type, such as ZSM-22, the MEL type, such as ZSM-11, the FER type. Other suitable zeolites are for example zeolites of the STF-type, such as SSZ-35, the SFF type, such as SSZ-44 and the EU-2 type, such as ZSM-48.

As mentioned above, where the SAPO and A1PO type molecular sieves have phosphorus as a part of their molecular sieve structure, zeolite-comprising molecular sieve catalyst will comprise phosphorus as such or in a compound, i.e. phosphorus other than any phosphorus included in the framework of the molecular sieve. The phosphorus may be introduced by pre-treating the zeolites prior to formulating the catalyst and/or by post-treating the formulated catalyst comprising the zeolites. Preferably, a catalyst comprising zeolites comprises phosphorus as such or in a compound in an elemental
amount of from 0.05 - 10 wt% based on the weight of the formulated catalyst.

Preferred phosphorus-comprising molecular sieve catalyst are catalyst comprising SAPO-34 and/or phosphorus combined with one or both of ZSM-5 and ZSM-11 zeolites.

In addition to the molecular sieves, the phosphorus-comprising molecular sieve catalyst compositions typically also include binder materials, matrix material and optionally fillers. Suitable matrix materials include clays, such as kaolin. Suitable binder materials include silica, alumina, silica-alumina, titania and zirconia.

A particular advantage of using the phosphorus-comprising molecular sieve catalyst as described herein above is that molecular sieve in the catalyst is able to absorb significant amounts of water. This makes the resulting fertilizer composition particularly suitable for use in arid environments, where it is required to hold the little water available inside the substrate as long as possible. Additional benefits of the water absorbing capacity of the described molecular sieves are that the water will aid in releasing and transporting the phosphor and, when present, other nutrients from the molecular sieve to the plant material, as well as causing the molecular sieve to decompose. Many molecular sieve structures are sensitive to water and decompose when in prolonged contact with water. The latter effect will further improve the release of the phosphorus. As the decomposition of the molecular sieve structure is a slow process, the release of the phosphorus is also slow allowing the fertilizer composition to release phosphorus for prolonged times.
The fertilizer composition may comprise other components that may aid the fertilizer function or improve the distribution or handling of the fertilizer. A preferred component which may be comprised in the fertilizer composition is sulphur. As mentioned above, sulphur is one of the macronutrients required for plant growth. The sulphur may be present in elemental form or as a compound. Although, typically sulphur is not present in spent phosphorus-comprising molecular sieve catalyst obtained from a MTO process, it may be added to the fertilizer composition. It may be added to the fertilizer composition separately from the spent phosphorus-comprising molecular sieve catalyst, however, preferably, the sulphur is added to the fertilizer by depositing the sulphur on the spent phosphorus-comprising molecular sieve catalyst.

Another, preferred component which may be comprised in the fertilizer composition is carbonaceous material. The presence carbonaceous material may be of use when herbicides and pesticides are used in the plant growing process. Although, these substances serve a clear purpose when growing plants or crops, it is undesirable that these substances move freely through the subsurface or substrate. The carbonaceous material may act as an adsorbent for such substances, thereby immobilizing the herbicides and pesticides. In addition, the carbonaceous material may serve as an adsorbent for many heavy metal containing organic complexes.

One particular useful application of the fertilizer composition according to the invention, where the fertilizer composition comprises carbonaceous material, is where the fertilizer composition is applied as a separate layer below a top substrate layer. In this
embodiment the fertilizer layer may act as a barrier layer preventing at least part of the herbicides and pesticides substances to penetrate further into the substrate and contaminate lower levels of the substrate. After the fertilizer has been depleted, i.e. the phosphorus in the fertilizer has been depleted, the barrier layer may be separately removed and treated. Preferably, the carbonaceous material is present in the fertilizer composition as part of the spent phosphorus-comprising molecular sieve catalyst. During the methanol to olefin (MTO) process, carbonaceous deposits are formed in and on the phosphorus-comprising molecular sieves catalyst. Typically, in a MTO process the phosphorus-comprising molecular sieves catalyst is periodically treated (or regenerated) to remove part of the carbonaceous deposits, which lead to a reversible deactivation of the phosphorus-comprising molecular sieves catalyst. This treatment or regeneration step comprises an oxidative removal of the carbonaceous deposits by contacting the phosphorus-comprising molecular sieves catalyst comprising carbonaceous deposits with air at elevated temperatures. Although this treatment restores the activity of the phosphorus-comprising molecular sieves catalyst by removing excess carbonaceous deposits, repetitive exposure to the conditions prevailing in the regeneration step leads to a non-reversible deactivation of the phosphorus-comprising molecular sieves catalyst. As a result, part of the catalyst is withdrawn from the MTO process as spent phosphorus-comprising molecular sieves catalyst. Preferably, the phosphorus-comprising molecular sieves catalyst withdrawn from the MTO process as spent
phosphorus-comprising molecular sieves catalyst comprises carbonaceous deposits.

In another aspect, the present invention provides a process for preparing a fertilizer composition. In the process according to the invention, a phosphorus-comprising molecular sieve catalyst as described herein is provided for use in a MTO process to prepare lower olefins by contacting the catalyst with a feedstock comprising methanol and optionally steam to convert at least part of the methanol to ethylene and propylene. The catalyst and the feedstock are preferably contacted at a temperature of 350 to 750 °C, more preferably 450 to 700°C, even more preferably 500 to 650°C; and a pressure from 0.1 kPa (1 mbar) to 5 MPa (50 bar), preferably from 100 kPa (1 bar) to 1.5 MPa (15 bar).

During the conversion of methanol to lower olefins, carbonaceous deposits are formed on the catalyst, which may lead to a reversible deactivation of the catalyst. Periodically, the catalyst is regenerated by contacting the deactivated catalyst with an oxygen-containing gas, preferably air or oxygen enriched air, at a temperature in the range of from 580 to 800 °C, preferably in the range of from 600 to 750 °C, more preferably in the range of from 620 to 680 °C, and a pressure in the range of from 1 to 5 bara, preferably in the range of from 1 to 3 bara, more preferably in the range of from 1.3 to 2 bara.

It is not necessary to remove all the coke from the catalyst as it is believed that a small amount of residual coke may enhance the catalyst performance and additionally, it is believed that complete removal of the coke may also lead to degradation of the molecular sieve.

The MTO process and the regeneration of the catalyst can suitably be carried out in a fixed bed, a fluidized
bed such as a dense, turbulent or fast fluidized bed, or in a riser or downward regenerator. Preferably, the regeneration is carried out in a turbulent fluidized bed.

The phosphorus-comprising molecular sieve catalyst is subjected to one or more methanol-to-olefin conversion, or MTO, and catalyst regeneration cycles. As a result, part of the catalyst will become irreversibly deactivated and at least part of the phosphorus-comprising molecular sieve catalyst is withdrawn from the process as spent phosphorus-comprising molecular sieve catalyst. The phosphorus-comprising molecular sieve catalyst may be withdrawn directly following the MTO step or directly following the regeneration step. Phosphorus-comprising molecular sieve catalyst withdrawn directly following the MTO step will comprise more carbonaceous deposits compared to the phosphorus-comprising molecular sieve catalyst withdrawn directly following the regeneration step. Preferably, the catalyst is withdrawn directly following the regeneration step as the regeneration of the catalyst provides at least part of the heat required for the MTO process. The regenerated catalyst will still comprise carbonaceous deposits, albeit less than the phosphorus-comprising molecular sieve catalyst withdrawn directly following the MTO step.

The spent phosphorus-comprising molecular sieve catalyst withdrawn from the process is used to formulate a fertilizer composition comprising the phosphorus-comprising molecular sieve catalyst. The fertilizer composition may consist of the spent phosphorus-comprising molecular sieve catalyst alone or may comprises other components that may aid the fertilizer function or improve the distribution or handling of the fertilizer.
The spent phosphorus-comprising molecular sieve catalyst may be obtained in the form of spray dried catalyst particles, spheres, tablets, rings, extrudates, etc., depending on the form of the fresh phosphorus-comprising molecular sieve catalyst initially provided to the MTO process. In addition, the spent phosphorus-comprising molecular sieve catalyst may comprise catalyst fines and other smaller catalyst particles formed through attrition during the operation of the MTO process.

Depending on the desired size and shape of the spent phosphorus-comprising molecular sieve catalyst particles in the fertilizer composition, the spent phosphorus-comprising molecular sieve catalyst may to crushed or otherwise treated to reduce the catalyst particle size. Furthermore, the spent phosphorus-comprising molecular sieve catalyst may be filtered or otherwise treated to remove catalyst fines that are undesirably small.

Any iron particles present in the spent phosphorus-comprising molecular sieve catalyst may be removed by means of magnetic separation. Such iron particles may be introduced in the spent phosphorus-comprising molecular sieve catalyst due to friction between the reactor walls and the phosphorus-comprising molecular sieve catalyst in the MTO process. Such iron particles may be removed, however, in small amounts iron is a micronutrient that is preferably present in the fertilizer composition next to the phosphorus.

As mentioned herein above, also sulphur is a valuable nutrition. Preferably, the fertilizer composition also comprises sulphur, in elementary form or as a sulphur compound. Preferably, the prior to formulating the fertilizer composition, the spent phosphorus-comprising molecular sieve catalyst is contacted with a sulphur-
containing compound and subsequently calcining the contacted spent phosphorus-comprising molecular sieve catalyst. Suitable sulphur-containing compounds include compounds selected from the group consisting of H₂SO₄, H₂SO₃, H₂SO₇, Na₂SO₄, and (NH₄)₂SO₄. The spent phosphorus-comprising molecular sieve catalyst may be impregnated with the sulphur-containing and subsequently calcined. A method for addition of sulphur to molecular sieves and molecular sieve comprising catalyst that may be used for addition of sulphur to the spent phosphorus-comprising molecular sieve catalyst of the present invention is described in US20120142990, which is hereby incorporated by reference.

If desired additional phosphorous may be added to the spent catalyst.

As mentioned herein above, a benefit of the present invention, wherein a spent phosphorus-comprising molecular sieve catalyst obtained from a process for converting methanol to olefins is used, is that the spent phosphorus-comprising molecular sieve catalyst used does not comprise significant amounts of heavy metals. Preferably, at least part, preferably all, of the methanol used as feedstock for the MTO process is derived from biomass. The biomass will contain trace amounts of metals naturally present in the plant material used to generate the biomass. The presence of such trace metals is preferred as they act as micronutrients to plant growth.

In a further aspect, the invention provides a method to introduce phosphorus to a substrate to promote plant growth, comprising applying a fertilizer composition according to the invention to a substrate used to grow plants.
In a preferred embodiment of this method, the fertilizer comprises carbonaceous material and the fertilizer is applied as a separate layer below a top layer of substrate. As mentioned above, such a separate layer of carbonaceous material-comprising fertilizer composition may aid in the capture of herbicides and pesticides and potentially other toxic components.
CLAIMS

1. A fertilizer composition comprising spent phosphorus-comprising molecular sieve catalyst obtained from a process for converting methanol to olefins.
2. A fertilizer composition according to claim 1, wherein the phosphorus-comprising molecular sieve catalyst comprises catalyst comprising SAPO-34 and/or phosphorus combined with one or both of ZSM-5 and ZSM-11 zeolites.
3. A fertilizer composition according to claim 1 or 2, wherein the molecular sieve further comprises carbonaceous deposits.
4. A fertilizer composition according to any one of the preceding claims, wherein the fertilizer composition further comprises sulphur of a sulphur-comprising compound.
5. A fertilizer composition according to claim 4, wherein the molecular sieve further comprises sulphur of a sulphur-comprising compound.
6. A process for preparing a fertilizer composition, comprising:
   i) providing a phosphorus-comprising molecular sieve catalyst;
   ii) subjecting the catalyst to one or more methanol-to-olefin conversion and catalyst regeneration cycles;
   iii) withdrawing at least part of the catalyst as spent phosphorus-comprising molecular sieve catalyst;
   iv) formulating a fertilizer composition comprising the spent phosphorus-comprising molecular sieve catalyst.
7. A process according to claim 6, wherein prior to formulating the fertilizer composition the spent phosphorus-comprising molecular sieve catalyst is contacted with a sulphur-containing compound and subsequently calcining the contacted spent phosphorus-comprising molecular sieve catalyst.

8. A process according to claim 6 or 7, wherein prior to step iv) the spent phosphorus-comprising molecular sieve catalyst is treated to remove iron.

9. A process according to any one of claims 6 to 8, wherein the phosphorus-comprising molecular sieve catalyst is withdrawn from the process directly following catalyst regeneration.

10. A process according to any one of claims 6 to 9, wherein the methanol is derived from biomass or synthesis gas.

11. A method to introduce phosphorus to a substrate to promote plant growth, comprising applying a fertilizer composition according to any one of claims 1 to 5 to a substrate used to grow plants.

12. A method according to claim 11, wherein the fertilizer composition comprises carbonaceous material and the fertilizer composition is applied as a separate layer below a top layer of substrate.
**A. CLASSIFICATION OF SUBJECT MATTER**

ADD. C05B17/00

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

**B. FIELDS SEARCHED**

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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[X] Further documents are listed in the continuation of Box C.  

[X] See patent family annex.

**Date of the actual completion of the international search**  
28 April 2014

**Date of mailing of the international search report**  
08/05/2014

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Authorized officer:  
Rodriguez Fontao, M
**DOCUMENTS CONSIDERED TO BE RELEVANT**

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