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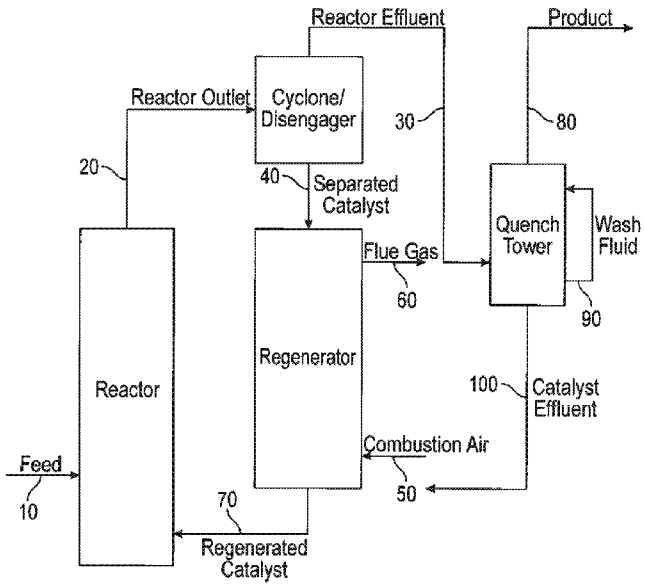


FIGURE 1

(57) Abstract: A paraffin having 2-8 carbon atoms may be dehydrogenated by contacting the paraffin with metal oxide cataiyst(s) to produce light olefins, such as propylene, under certain reaction conditions in a riser, fluidized bed, or fixed-bed swing reactor. The resulting metal oxide catalyst fines contained in the reactor effluent stream formed by the dehydrogenation reaction may be recovered by contacting the reactor effluent stream with a wash fluid to form a catalyst effluent stream that is subsequently slurried and filtered to capture the catalyst fines for potential reuse.

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[Continued on next page]

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PROCESSES FOR CATALYTIC PARAFFIN DEHYDROGENATION AND CATALYST RECOVERY

TECHNICAL FIELD

[0001] The present invention relates to a process for dehydrogenation of paraffins by reacting a paraffin stream with metal oxide catalyst(s) to produce light olefins, such as propylene, and a process for the recovery of metal oxide catalyst fines from the reactor effluent stream using a wash fluid and filtration.

BACKGROUND

[0002] The abundance of alkanes and paraffins from shale and stranded gas has spurned the development of more cost-effective ways to produce light olefins, the demand for which has increased significantly in recent years. Steam cracker units using lighter shale condensates as feedstock have been used to meet to the increase in the demand for light olefins, like ethylene. However, these units have been found to be deficient for propylene production due to the low propylene/ethylene ratio and low propylene yield. As a result, finding routes for the targeted production of propylene have received considerable interest.

[0003] It has been shown that catalytic dehydrogenation provides the possibility of high selectivity to a single olefin product. Current alkane dehydrogenation processes for the production of propylene and other light olefins employ the use of platinum-based and chromium-based catalysts. Given the expense associated with platinum and the carcinogenic properties of chromium, there is a need for developing less expensive, less toxic metal oxide catalysts that can is capable of good alkene selectivity during the dehydrogenation process and a correspondingly high yield.

[0004] A potential deficiency in processes for alkane or paraffin dehydrogenation employing a riser or fluidized-bed type reactor is the amount of catalyst fines in the effluent streams leaving the dehydrogenation reactor. With regard to the reactor effluent stream, a water quench tower is used to cool the reactor effluent and condense the water therein, particularly if dilution steam is used to lower

the partial pressure of the alkane or paraffin. The catalyst fines contained in the reactor effluent stream cannot easily be separated from quench water, leading to excessive fouling in the equipment and consequential high maintenance costs. Thus, there is also a need for improved recovery of catalyst fines found in the effluent stream from the dehydrogenation reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] The FIGURE 1 is a schematic illustration of a process for catalytic paraffin dehydrogenation and catalyst recovery of the kind described herein.

SUMMARY

[0006] There is provided, in one form, a process for dehydrogenating paraffins by contacting a metal oxide catalyst with a paraffin having 2-8 carbon atoms in a riser, fluidized bed, or fixed-bed swing reactor for a reaction period ranging from about 0.05 seconds to about 10 minutes. In one embodiment, the metal oxide catalyst is selected from group consisting of oxides of zinc, titanium, copper, iron, manganese, aluminum, silicon, zirconium, cerium, dysprosium, erbium, europium, gadolinium, lanthanum, neodymium, praseodymium, samarium, terbium, ytterbium, yttrium, niobium, and combinations thereof, wherein the metal oxide catalyst is substantially free of platinum and chromium.

[0007] There is further provided in another form, a process for recovering catalyst fines from the reactor effluent stream of a catalytic paraffin dehydrogenation reaction in a riser or fluidized-bed type reactor, the process comprising: contacting a metal oxide catalyst with a paraffin having 2-8 carbon atoms; generating a reactor effluent stream comprising metal oxide catalyst fines after contacting the metal oxide catalyst with the paraffin; and contacting the reactor effluent stream with a wash fluid to transfer the metal oxide catalyst fines from the reactor effluent stream into the wash fluid and form a cooled catalyst effluent stream and a substantially catalyst-free product stream.

DETAILED DESCRIPTION

[0008] It has been discovered that contacting one or more metal oxide catalysts with a paraffin having 2-8 carbon atoms in a dehydrogenation reaction for a period ranging from about 0.05 seconds to about 10 minutes in a reactor may lead to better selectively for the production of certain olefins, such as propylene and ethylene. It has also been discovered that metal oxide catalyst fines, generated because of attrition in a riser or fluidized-bed type reactor, are contained within the reactor effluent stream. These catalyst fines may be recovered by contacting the effluent stream of the reactor with a wash fluid, typically oil or water, to form a cooled catalyst effluent stream and a substantially catalyst-free product stream and then filtering the cooled catalyst effluent stream with a set of filters to capture the catalyst fines for potential reuse.

[0009] In one embodiment, the paraffin to be contacted with the metal oxide catalyst(s) may be propane, ethane, n-butane, isobutane, and combinations thereof. In another embodiment, the paraffin may be introduced to the reactor with or without an inert diluent or steam.

[0010] The metal oxide catalysts useful in dehydrogenating the paraffin to produce a light olefin product gas may be made up of one or more of the following oxides: zinc, titanium, copper, iron, manganese, aluminum, silicon, zirconium, cerium, dysprosium, erbium, europium, gadolinium, lanthanum, neodymium, praseodymium, samarium, terbium, ytterbium, yttrium, or niobium. In a non-limiting embodiment, the metal oxide catalyst(s) used are substantially free of platinum and chromium.

[0011] The dehydrogenation of the paraffin using metal oxide catalysts of the kinds described above and recovery of catalyst fines in the reactor effluent stream may be accomplished, in one non-limiting embodiment, by the process depicted in the FIGURE 1 in which a paraffin feedstock 10 comprising paraffins having 2-8 carbons is contacted with one or more metal oxide catalysts in a riser or fluidized bed reactor under dehydrogenation conditions. This process may be performed at a reaction temperature of 500-800 °C, a space velocity of 0.1 -1 h^{-1}, and a pressure of 0.01-0.2 MPa. In one embodiment, the reaction period may range from about 0.05

seconds to about 10 minutes. In other non-limiting embodiments, the dehydrogenation reaction between the paraffin and the metal oxide catalyst(s) may also be carried out in a fixed-bed swing or riser or fluidized-bed reactor from which a reactor outlet stream 20 is formed. The reactor outlet stream 20, in one non-restrictive embodiment, is then sent to a cyclone or disengager to separate catalyst from the reactor outlet stream and form an overhead reactor effluent stream 30.

[0012] In a non-limiting embodiment, the reactor effluent stream 30 contains light olefins, such as, without limitation, propylene and/or ethylene. The bulk of the catalyst is retained within the reactor or recovered in the cyclone/disengager and then sent as a separated catalyst stream 40 to a regenerator, which uses combustion air 50 to produce a flue gas stream 60 and a regenerated catalyst stream 70 that is returned to the reactor.

[0013] However, some catalyst fines, formed due to attrition in reactor types like riser or fluidized-bed reactors, may be contained in the reactor effluent stream 30. These metal oxide catalyst fines may be recovered in a process in which the reactor effluent stream 30 is contacted in a quench tower with a wash fluid 90, typically oil or water, to transfer the metal oxide catalyst fines from the reactor outlet stream into the wash fluid and form a cooled catalyst effluent stream 100 and a substantially catalyst-free product stream 80. In one non-restrictive embodiment, the reactor effluent stream 30 is contacted with the wash fluid in a quench tower that contains vapor-liquid contacting elements, such as, without limitation, packing or trays. The quench tower, in another embodiment, may also have a recirculation loop for continuously recirculating a wash fluid to the contacting elements.

[0014] In another non-restrictive embodiment, the cooled catalyst effluent stream 100 may subsequently be converted into a slurry and then directed to one or more filters to separate the metal oxide catalyst fines. In one embodiment, the slurry is continuously passed through a first filter in a filtration mode to separate the metal oxide catalyst fines therefrom while a second filter in parallel with the first filter is in backflushing mode to remove the separated metal oxide catalyst fines therefrom. The filtration of the slurry may comprise periodically alternating the first and the second filters between filtration and backflushing mode. After filtration, the separated

metal oxide catalyst fines may be collected and accumulated in a catalyst accumulator. The catalyst fines may then be prepared for reuse in the dehydrogenation reaction.

[0015] In the foregoing specification, the invention has been described with reference to specific embodiments thereof. However, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, paraffins, metal oxide catalysts, dehydrogenation reaction conditions and equipment, and catalyst fine recovery conditions and equipment falling within the claimed or disclosed parameters, but not specifically identified or tried in a particular example, are expected to be within the scope of this invention.

[0016] The present invention may be practiced in the absence of an element not disclosed. In addition, the present invention may suitably comprise, consist or consist essentially of the elements disclosed. For instance, the process may comprise, consist of, or consist essentially of: contacting a metal oxide catalyst with a paraffin having 2-8 carbon atoms in a reactor for a reaction period ranging from about 0.05 seconds to about 10 minutes.

[0017] Alternatively, the recovery of the catalyst fines from a reactor effluent stream may comprise, consist of, or consist essentially of: contacting a metal oxide catalyst with a paraffin having 2-8 carbon atoms, generating a reactor effluent stream comprising metal oxide catalyst fines after contacting the metal oxide catalyst with the paraffin, and contacting the reactor effluent stream with a wash fluid to transfer the metal oxide catalyst fines from the reactor effluent stream into the wash fluid and form a cooled catalyst effluent stream and a substantially catalyst-free product stream.

[0018] The words "comprising" and "comprises" as used throughout the claims, are to be interpreted to mean "including but not limited to" and "includes but not limited to", respectively.

[0019] As used herein, the word "substantially" shall mean "being largely but not wholly that which is specified."

[0020] As used herein, the singular forms "a," "an," and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[0021] As used herein, the term "about" in reference to a given parameter is inclusive of the stated value and has the meaning dictated by the context (*e.g.*, it includes the degree of error associated with measurement of the given parameter).

[0022] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

CLAIMS

What is claimed is:

1. A process for dehydrogenating paraffins, the process comprising:
contacting at least one metal oxide catalyst with a paraffin having 2-8 carbon atoms for a reaction period ranging from about 0.05 seconds to about 10 minutes in a reactor.

2. The process of claim 1, wherein the reactor is a riser reactor, fluidized bed reactor, or a fixed-bed swing reactor.

3. The process of claim 1, wherein the paraffin is selected from a group consisting of propane, ethane, n-butane, isobutane, and combinations thereof.

4. The process of claim 1, further comprising generating a reactor effluent stream comprising an olefin.

5. The process of claim 4, wherein the olefin is selected from a group consisting of propylene, ethylene, and combinations thereof.

6. The process of claim 1, wherein the reaction occurs at a temperature ranging from about 500 °C to about 800 °C.

7. The process of claim 1, wherein the reaction occurs at a pressure ranging from about 0.01 MPa to about 0.02 MPa.

8. The method of claim 1, wherein the metal oxide catalyst is selected from a group consisting of oxides of zinc, titanium, copper, iron, manganese, aluminum, silicon, zirconium, cerium, dysprosium, erbium, europium, gadolinium, lanthanum, neodymium, praseodymium, samarium, terbium, ytterbium, yttrium, niobium, and combinations thereof.

9. The process of claim 2, wherein the metal oxide catalyst is substantially free of platinum and chromium.

10. The process of claim 8, wherein the paraffin is introduced to the reactor with an inert diluent or steam.

11. The process for recovering catalyst fines from a reactor effluent stream of a catalytic paraffin dehydrogenation reaction, the process comprising:
    a. contacting a metal oxide catalyst with a paraffin having 2-8 carbon atoms in a reactor;
    b. generating a reactor effluent stream comprising metal oxide catalyst fines after contacting with the metal oxide catalyst with the paraffin; and
    c. contacting the reactor effluent stream with a wash fluid to transfer the metal oxide catalyst fines from the reactor effluent stream into the wash fluid and form a cooled catalyst effluent stream and a substantially catalyst-free product stream.

12. The process of claim 11, further comprising converting the cooled catalyst effluent stream into a slurry.

13. The process of claim 12, further comprising directing the slurry to one or more filters to separate the metal oxide catalyst fines.

14. The process of claim 13, wherein the slurry is continuously passed through a first filter in a filtration mode to separate the metal oxide catalyst fines therefrom while a second filter in parallel with the first filter is in backflushing mode to remove the separated metal oxide catalyst fines therefrom.

15. The process of claim 14, wherein the filtration of the slurry comprises periodically alternating the first and the second filters between filtration and backflushing modes.

16. The process of claim 14, wherein the separated metal oxide catalyst fines are accumulated in a catalyst accumulator.

17. The process of claim 11, wherein the reactor effluent stream is contacted with the wash fluid in a quench tower.

18. The process of claim 17, wherein the quench tower has vapor-liquid contacting elements.

19. The process of claim 17, wherein the quench tower has a recirculation loop for continuously recirculating a wash oil to the contacting elements.

20. The process of claim 17, wherein the wash fluid comprises oil or water.

AMENDED CLAIMS
received by the International Bureau on 14 August 2020 (14.08.2020)

What is claimed is:

1. A process for dehydrogenating paraffins, the process comprising:
   contacting at least one metal oxide catalyst with a paraffin having 2-8 carbon atoms for a reaction period ranging from about 0.05 seconds to about 10 minutes in a reactor;
   wherein the paraffin is selected from a group consisting of propane, n-butane, isobutane, and combinations thereof;
   wherein the metal oxide catalyst is selected from a group consisting of oxides of zinc, titanium, copper, iron, manganese, aluminum, silicon, zirconium, cerium, dysprosium, erbium, europium, gadolinium, lanthanum, neodymium, praseodymium, samarium, terbium, ytterbium, yttrium, niobium, and combinations thereof; and
   wherein the metal oxide catalyst is substantially free of platinum and chromium.

2. The process of claim 1, wherein the reactor is a riser reactor, fluidized bed reactor, or a fixed-bed swing reactor.

3. The process of claim 1, further comprising generating a reactor effluent stream comprising an olefin.

4. The process of claim 3, wherein the olefin is selected from a group consisting of propylene, ethylene, and combinations thereof.

5. The process of claim 1, wherein the reaction occurs at a temperature ranging from about 500 °C to about 800 °C.

6. The process of claim 1, wherein the reaction occurs at a pressure ranging from about 0.01 MPa to about 0.02 MPa.

7. The process of claim 1, wherein the paraffin is introduced to the reactor with an inert diluent or steam.

8. A process for recovering catalyst fines from a reactor effluent stream of a catalytic paraffin dehydrogenation reaction, the process comprising:
    a. contacting a metal oxide catalyst with a paraffin having 2-8 carbon atoms in a reactor, where
        i. wherein the paraffin is selected from a group consisting of propane, n-butane, isobutane, and combinations thereof;
        ii. wherein the metal oxide catalyst is selected from a group consisting of oxides of zinc, titanium, copper, iron, manganese, aluminum, silicon, zirconium, cerium, dysprosium, erbium, europium, gadolinium, lanthanum, neodymium, praseodymium, samarium, terbium, ytterbium, yttrium, niobium, and combinations thereof; and
        iii. wherein the metal oxide catalyst is substantially free of platinum and chromium;
    b. generating a reactor effluent stream comprising metal oxide catalyst fines after contacting with the metal oxide catalyst with the paraffin; and
    c. contacting the reactor effluent stream with a wash fluid to transfer the metal oxide catalyst fines from the reactor effluent stream into the wash fluid and form a cooled catalyst effluent stream and a substantially catalyst-free product stream.

9. The process of claim 8, further comprising converting the cooled catalyst effluent stream into a slurry.

10. The process of claim 9, further comprising directing the slurry to one or more filters to separate the metal oxide catalyst fines.

11. The process of claim 10, wherein the slurry is continuously passed through a first filter in a filtration mode to separate the metal oxide catalyst fines therefrom while a second filter in parallel with the first filter is in backflushing mode to remove the separated metal oxide catalyst fines therefrom.

12. The process of claim 11, wherein the filtration of the slurry comprises periodically alternating the first and the second filters between filtration and backflushing modes.

13. The process of claim 11, wherein the separated metal oxide catalyst fines are accumulated in a catalyst accumulator.

14. The process of claim 8, wherein the reactor effluent stream is contacted with the wash fluid in a quench tower.

15. The process of claim 14, wherein the quench tower has vapor-liquid contacting elements.

16. The process of claim 14, wherein the quench tower has a recirculation loop for continuously recirculating a wash oil to contacting elements.

17. The process of claim 14, wherein the wash fluid comprises oil or water.

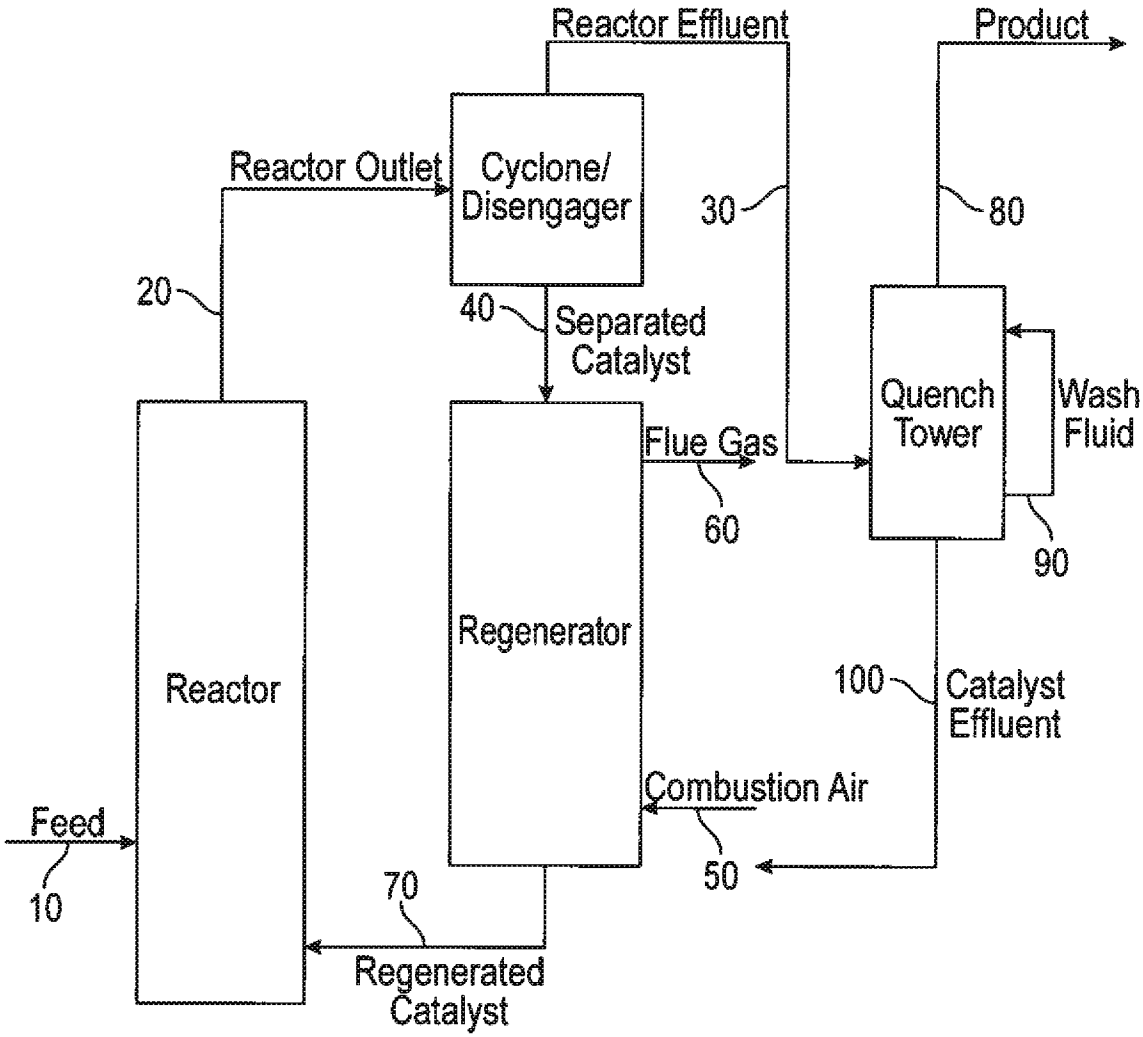

Reactor Effluent
Product
Reactor Outlet
Cyclone/
Disengager
30
80
20
40
Separated
Catalyst
Quench
Tower
Wash
Fluid
Flue Gas
60
90
Regenerator
Reactor
100
Catalyst
Effluent
Combustion Air
Feed
50
10
70
Regenerated
Catalyst

FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US20/23627

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C07C 5/32, 5/333; B01J 23/92 (2020.01)

CPC - C07C 5/322, 5/3332; B01J 23/92

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)
See Search History document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2014/0371504 A1 (UOP LLC) 18 December 2014; figure 4; paragraphs [0024], [0029], [0032]-[0033], [0045], [0050], [0059], [0068], [0083], [0086]	1-6, 11-13, 17, 20 -- 14-16, 18-19
X	US 2017/0210685 A1 (NOVA CHEMICALS) 27 July 2017; paragraphs [0026]-[0029], [0034]; claim 1	1-2, 7-9
X	WO 03/026787 A2 (CONOCO INC.) 03 April 2003; abstract; page 3, lines 24-27; page 4, lines 1-15; page 5, line 31 to page 6, line 2; page 7, lines 18-21; page 8, Table 1	1, 8, 10
Y	US 7,011,740 B2 (TALLMAN, M et al.) 14 March 2006; figure 1; column 2, lines 7-19; column 8, lines 4- 20	14-16, 18-19
X	GB 815,332 A (ESSO RESEARCH AND ENGINEERING COMPANY) 24 June 1959; entire document	1
X, P	US 2020/0101445 A1 (EXELUS, INC et al.) 02 April 2020; entire document	1

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"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	Date of mailing of the international search report
05 May 2020 (05.05.2020)	11 JUN 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas Telephone No. PCT Helpdesk: 571-272-4300