



(51) International Patent Classification:

B01J 37/08 (2006.01) **B01J 37/02** (2006.01)
B01J 23/86 (2006.01)

(21) International Application Number:

PCT/IB2017/053712

(22) International Filing Date:

21 June 2017 (21.06.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/353,094 22 June 2016 (22.06.2016) US

(71) Applicant: **SABIC GLOBAL TECHNOLOGIES B.V.**
[NL/NL]; Plasticslaan 1, 4612 PX Bergen op Zoom (NL).

(72) Inventors: **CHOI, YongMan**; P.O. Box 5101, Riyadh,
11422 (SA). **BUNAMA, Ramsey**; P.O. Box 5101, Riyadh,
11422 (SA). **EL-YAHYAOU, Khalid Mohammed**; P.O.
Box 5101, Riyadh, 11422 (SA).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,
KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: CONVERSION OF DEACTIVATED CHROMIA-BASED CATALYSTS

(57) Abstract: A method for generating supported metal chromium oxide catalysts includes providing a deactivated chromium-based catalyst; determining the amount of chromium in the deactivated chromium-based catalyst by inductively coupled plasma atomic emission spectroscopy; combining a calculated amount of a metal material with the deactivated chromium-based catalyst to form a mixture, wherein the calculated amount is based on the determined amount of chromium in the deactivated chromium-based catalyst to yield a desired stoichiometry of the metal chromium oxide catalyst; drying the mixture at a temperature of at least 100 °C; and calcining the dried mixture at a temperature of at least 250 °C to form the metal chromium oxide catalysts.



CONVERSION OF DEACTIVATED CHROMIA-BASED CATALYSTS

BACKGROUND

[0001] The CATOFIN® process converts aliphatic hydrocarbons to their corresponding olefins over a fixed-bed chromia alumina catalyst. For example, it can be used to produce isobutylene, propylene or isoprene from isobutane, propane or isopentane, respectively. The process is an adiabatic, cyclic process. Each cycle comprises several steps, including catalyst reduction, dehydrogenation, purging of the remaining hydrocarbon from the reactor, and finally a regeneration step with air. The cycle then starts again with the reduction step.

[0002] The dehydrogenation reaction is highly endothermic. Therefore, the temperature of the catalyst bed decreases during the dehydrogenation step. This decrease in temperature causes a decrease in paraffin conversion. In order to reheat the catalyst bed and remove coke that has deposited on the catalyst during the dehydrogenation step, the reactor is typically purged of hydrocarbon and then undergoes a regeneration step with air. Heat is provided to the bed by the hot air that passes through the bed and also by the combustion of the coke deposits on the catalyst. Reduction of the catalyst, with a reducing gas such as hydrogen, prior to dehydrogenation step also provides some additional heat. As flow in the reactor is usually from top to bottom and coke deposits to a larger amount at the reactor inlet, there is a tendency for the top of the bed to be hotter than the bottom of the bed. Also, the coke distribution in the catalyst bed, which is not easily controlled, affects the amount of heat added at each location and the resulting catalyst bed temperature profile. These factors make control of the temperature profile in the bed difficult. Hydrothermal stability of catalysts used in the CATOFIN® process is usually the limiting factor for their lifetime use. Thermal stability as well as high selectivity to the olefin are desired qualities.

[0003] Chromium-based catalysts used in CATOFIN® process are often regenerated with heat-generating materials (HGM) used in CATOFIN® reactors. For example, the catalysts are physically mixed with the heat-generating materials to transfer the extra heat released from the reduction and oxidation reactions of heat-generating materials with reducing gases (such as H₂, CH₄, and CO) and oxidizing gases (such as air). The primary heat-generating materials include CuO and Cu. The extra heat is transferred to the endothermic dehydrogenation of hydrocarbons on chromium-based catalysts, which improves the yield. However, owing to unexpected chemical reactions, the copper and chromium

based components from the heat-generating materials and the catalysts are fused, actually resulting in deactivation of the catalysts and heat-generating materials.

[0004] Despite multiple regenerations, eventually the deactivated catalysts used will need to be discarded and replaced with a new catalyst. However, discarding the deactivated chromium-based catalysts may introduce various environmental issues. Therefore, there is a need to recycle the deactivated chromium-based catalysts into new catalyst systems for further use to avoid the detrimental environmental issues associated with discarding the deactivated catalyst.

BRIEF DESCRIPTION

[0005] The above described and other features are exemplified by the following detailed description.

[0006] A method for generating supported metal chromium oxide catalysts, comprises: providing a deactivated chromium-based catalyst; determining the amount of chromium in the deactivated chromium-based catalyst by inductively coupled plasma atomic emission spectroscopy; combining a calculated amount of a metal material with the deactivated chromium-based catalyst to form a mixture, wherein the calculated amount is based on the determined amount of chromium in the deactivated chromium-based catalyst to yield a desired stoichiometry of the metal chromium oxide catalyst; drying the mixture at a temperature of at least 100 °C; and calcining the dried mixture at a temperature of at least 250 °C to form the metal chromium oxide catalysts

[0007] A method for generating a supported metal chromium oxide catalyst, comprising: combining a deactivated chromium-based catalyst with a copper oxide based heat generating material to form a mixture; drying the mixture at a temperature of at least 100 °C; and calcining the dried mixture at a temperature of at least 250 °C to form the supported metal chromium oxide catalyst.

DETAILED DESCRIPTION

[0008] The present disclosure provides methods for generating a supported metal chromium oxide catalyst. For example, the present methods can be used to generate copper chromium oxides. The metal chromium oxide catalyst can be of the formula $\text{Cu}_x\text{Cr}_y\text{O}_z$, wherein x is 1 to 2, y is 1 to 2, and z is 4 to 5. Specific examples of the metal chromium oxide catalysts that can be generated include CuCrO_4 , CuCr_2O_4 , Cu_2CrO_4 , and $\text{Cu}_2\text{Cr}_2\text{O}_5$,

among others. Copper chromite, CuCr_2O_4 , for example, can be used for various high-value applications in the petrochemical industry, such as hydrogenation, dehydrogenation, hydrogenolysis, oxidation, alkylation, and cyclization. In addition, the present methods can be used to regenerate the deactivated chromium-based catalysts with heat-generating materials, which avoid merely fusing the heat-generating materials and chromium-based catalysts together, which results in further deactivation of the catalysts.

[0009] For example, the method can include providing a deactivated chromium-based catalyst and determining the amount of chromium in the deactivated chromium-based catalyst by inductively coupled plasma atomic emission spectroscopy. Based on the amount of chromium in the deactivated chromium-based catalyst, the amount of a heat generating material and/or metal can be calculated to yield a desired stoichiometry of the metal chromium oxide catalyst (e.g., M, Cr). In other words, the specific metal chromium oxide catalyst can be synthesized based on the molar ratio used of chromium and metal, such as copper or nickel, used during the mixing step. The desired stoichiometry of the metal chromium oxide catalyst can be a 5:1 molar ratio of metal to chromium to a 1:5 molar ratio of metal to chromium. For example, a desired stoichiometry of the metal chromium oxide catalyst can be a 1:1 molar ratio of metal to chromium.

[0010] The deactivated chromium-based catalyst and calculated amount of metal can be combined to form a mixture that is dried at a temperature of at least $100\text{ }^\circ\text{C}$, and then can be calcined at a temperature of at least $250\text{ }^\circ\text{C}$ to form the metal chromium oxide catalysts. The dried mixture can be calcined at a temperature of $300\text{--}600\text{ }^\circ\text{C}$, for example, $600\text{ }^\circ\text{C}$.

[0011] The heat generating material can be a heat releasing material. The heat releasing material can be any desirable material that releases heat during reduction and regeneration processes. For example, the heat releasing material may be copper oxide and/or nickel oxide, among others. The deactivated chromium-based catalyst can include a chromium oxide dehydrogenation catalyst manufactured on an alumina support. For example, the deactivated chromium-based catalyst can include Cr_2O_3 and Al_2O_3 .

[0012] In addition to chromium, it is envisaged that the catalyst may be adapted to incorporate other metals or metal oxide catalysts. Examples of metals or metal oxides thereof include, but are not limited to, aluminum, magnesium, zirconium, titanium, vanadium, nickel, rhodium, rhenium, iron, silicon, molybdenum, thorium, manganese, cerium, silver, lead, cadmium, calcium, antimony, tin, bismuth, cobalt, tungsten, and zinc.

[0013] Further, it is envisaged that the dehydrogenation catalyst may be adapted to incorporate dehydrogenation catalysts, in lieu of the Cr, such as zeolites, acid treated metal oxides (e.g. acid treated alumina), or acid treated clays. Zeolites are microporous, aluminosilicate minerals. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite. Synthetic catalysts may include composites of silica and alumina or other metal oxides, including silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, silicavanadia, as well as ternary combinations such as silica-alumina-magnesia, silica-alumina-zirconia, and silica-magnesia-zirconia. Other bifunctional catalysts include, platinum and/or rhodium doped zeolites, and platinum-alumina. Acid treated natural clays which may be desirable for use as the catalyst include kaolins, sub-bentonites, montmorillonite, fullers earth, and halloysite.

[0014] In one embodiment, the heat transfer media is copper. In one embodiment, the copper heat transfer material may be in a reduced state, i.e. elemental copper. Alternatively, the copper present in the dehydrogenation catalyst bed composition may be in a higher oxidation state (e.g. Cu^{1+} or Cu^{2+}). When in a higher oxidation state, the copper may be in an oxide form, for example CuO. Cu of the present process is selected as heat transfer media because it can easily oscillate between higher and lower oxidation states and produce heat during both oxidation and reduction reactions, whereby the heat generated may be utilized in subsequent dehydrogenation reactions. It is envisaged that the present process may be adapted to incorporate other heat releasing media, in lieu of, or in addition to Cu, wherein the heat releasing media is inert to dehydrogenation reactions. Other such heat releasing media may include, but is not limited to, silver, gold, aluminum, tungsten, platinum, etc., as long as it is inert to the dehydrogenation reaction and to produce heat from the reduction and regeneration processes.

[0015] The dehydrogenation catalyst can comprise 1 wt% to 20 wt%, for example, 1 wt% to 10 wt% or 5 wt% to 15 wt% of the heat transfer media relative to the total weight of the dehydrogenation catalyst.

[0016] For purposes of the present process, the catalyst can include a support which refers to a high surface area material to which a catalyst is affixed. The support may be inert or may participate in catalytic reactions. In the present process, the catalyst support can be inert to the dehydrogenation reaction. The reactivity of heterogeneous catalysts and nanomaterial-based catalysts occurs at the surface atoms. Consequently great effort is made

to maximize the surface area of a catalyst by distributing it over the support. Typical supports include various kinds of carbon, alumina, and silica. In one embodiment, the catalyst support is aluminum oxide. The catalyst support may be comprised of a plurality of different crystallographic phases. Therefore, in terms of alumina, the catalyst support may comprise α - Al_2O_3 , γ - Al_2O_3 , η - Al_2O_3 , θ - Al_2O_3 , χ - Al_2O_3 , κ - Al_2O_3 , and δ - Al_2O_3 , or a combination comprising at least one of the foregoing, for example, the catalyst support is γ - Al_2O_3 , or the catalyst support is α - Al_2O_3 .

[0017] In terms of the present process, an important characteristic of the catalyst support is its ability to store and distribute heat to aid in the catalytic process. One measure of the ability to distribute heat is the thermal conductivity. Heat transfer occurs at a higher rate across materials of high thermal conductivity than across materials of low thermal conductivity. One measure of the ability to store heat is the specific heat capacity. Heat capacity is a measurable physical quantity equal to the ratio of the heat added to (or subtracted from) an object to the resulting temperature change. Heat capacity is an extensive property of matter, meaning it is proportional to the size of the system. When expressing the same phenomenon as an intensive property, the heat capacity is divided by the amount of substance, mass, or volume, so that the quantity is independent of the size or extent of the sample. The specific heat capacity, therefore, is the heat capacity per unit mass of a material. Temperature reflects the average randomized energy of constituent particles of matter (e.g. atoms or molecules), while heat is the transfer of thermal energy across a system boundary into the body or from the body to the environment. Translation, rotation, and a combination of the two types of energy in the vibration (kinetic and potential) of atoms represent the degrees of freedom of motion which classically contribute to the heat capacity of matter. On a microscopic scale, each system particle absorbs thermal energy among the few degrees of freedom available to it, and at sufficient temperatures, this process contributes to the specific heat capacity. Therefore, a catalyst support with a high specific heat capacity, such as Al_2O_3 , is advantageous.

[0018] The mixing of the deactivated chromium-based catalyst with the heat generating material can be performed via a wet impregnation method or a solid state method. In an example, the mixing is performed via a wet impregnation method, wherein the heat generating material is copper. The copper can be provided by a precursor of copper nitrate. In an example, the deactivated chromium-based catalyst is mixed with the heat generating material via a solid state method, wherein the heat generating material is copper oxide.

[0019] In an example, deactivated chromium-based catalysts including Cr_2O_3 can be crushed to powder to increase the interaction with a second metal such as copper. The powder catalysts can be mixed with a copper-containing material by means of wet impregnation with copper nitrate or with copper oxide for the solid-state reaction. Before adding the second metal component, the powder catalyst can be characterized to determine the amount of chromium content, for example, using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique. The molar ratio of chromium to copper can be prepared based on the desired product. After the copper containing compound is mixed with the powder catalyst, a drying process at 120 °C can be performed for 24 hours, followed by calcination at 300 °C for at least 6 hours to produce the final metal chromium oxide catalyst.

[0020] The generated metal chromium oxide catalysts, including copper chromium oxide catalysts, can be used in a wide variety of applications. For example, copper chromium catalysts can be used in hydrogenation reactions to produce fatty alcohols. Copper oxide-chromium oxide catalysts can also be used in the detoxification of exhaust gases, in particular from automobile engines that contain aluminum, chromium, and copper oxide as substantial components. The generated copper chromite catalysts can also be used in the oxidation of oxidizable hydrocarbons and carbon monoxide present in the exhaust gases of internal combustion engines.

Examples

[0021] In an example, CuO was deposited on $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ using a wet impregnation method. An appropriate amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in a minimum amount of distilled water such that the molar ratio of Cr to Cu was 1:1, when mixed with $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ powder. After mixing, the mixture was dried for 12 hours at 120 °C in an oven. Inductively coupled plasma atomic emission spectroscopy technique was used to confirm the deposition amount of CuO on $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, which was found to be 4.23 wt% Cr and 2.58 wt% Cu. In situ X-ray diffractometer experiments were performed in air from room temperature to 1100 °C to examine the Cr and Cu oxide formation region.

Table 1: Summary of Reaction Conditions and Results	
Base material	$\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$
Deposited element	Cu using the wet impregnation method
Molar ratio of Cr : Cu	1 : 1
Condition	Drying at 120 °C for 24 hours
Composition of Cr and Cu	4.23 wt% (Cr) vs. 2.58 wt% (Cu)

In situ XRD conditions	Room temperature to 600 °C at 1 atmosphere
(Cr, Cu) oxide formation region	> 200°C
Final form of the (Cr, Cu) oxide	CuCrO ₄

[0022] As illustrated in Table 1, the formation of the copper chromium oxides was detected after 200 °C. As expected with the 1:1 molar ratio of copper to chromium, CuCrO₂ and CrCrO₄ coexisted at low temperature. However, when the temperature was above 600 °C, the CuCrO₂ was converted to CuCrO₄.

[0023] The supported copper chromium oxide catalysts were successfully prepared by the reaction of copper and Cr₂O₃/Al₂O₃. Further, various metal chromium-based oxide catalysts can be synthesized based on the molar ratio used of copper to chromium.

[0024] The method disclosed herein includes at least the following embodiments:

[0025] Embodiment 1: A method for generating supported metal chromium oxide catalysts, comprising: providing a deactivated chromium-based catalyst; determining the amount of chromium in the deactivated chromium-based catalyst by inductively coupled plasma atomic emission spectroscopy; combining a calculated amount of a metal material with the deactivated chromium-based catalyst to form a mixture, wherein the calculated amount is based on the determined amount of chromium in the deactivated chromium-based catalyst to yield a desired stoichiometry of the metal chromium oxide catalyst; drying the mixture at a temperature of at least 100 °C; and calcining the dried mixture at a temperature of at least 250 °C to form the metal chromium oxide catalysts.

[0026] Embodiment 2: The method of Embodiment 1, further comprising combining the deactivated chromium-based catalyst with the metal material via a wet impregnation method, wherein the metal material includes copper nitrate.

[0027] Embodiment 3: The method of any of Embodiments 1-2, further comprising combining the deactivated chromium-based catalyst with the metal material via a solid state method, wherein the metal material includes copper oxide.

[0028] Embodiment 4: The method of any of Embodiments 1-3, further comprising combining the deactivated chromium-based catalyst with the metal material via a solid state method, wherein the metal material includes nickel oxide.

[0029] Embodiment 5: The method of any of Embodiments 1-4, wherein the metal chromium oxide catalyst is a copper chromium oxide of the formula Cu_xCr_yO_z, wherein x is 1 to 2, y is 1 to 2, and z is 4 to 5.

[0030] Embodiment 6: The method of any of Embodiments 1-5, wherein the dried mixture is calcined at a temperature of 600 °C, wherein the metal chromium oxide catalyst is CuCrO_4 .

[0031] Embodiment 7: The method of Embodiment 6, wherein the dried mixture is calcined at a temperature of 600 °C.

[0032] Embodiment 8: The method of any of Embodiments 1-7, wherein a desired stoichiometry of the metal chromium oxide catalyst is a 1:1 molar ratio of metal to chromium.

[0033] Embodiment 9: A method for generating a supported metal chromium oxide catalyst, comprising: combining a deactivated chromium-based catalyst with a copper oxide based heat generating material to form a mixture; drying the mixture at a temperature of at least 100 °C; and calcining the dried mixture at a temperature of at least 250 °C to form the supported metal chromium oxide catalyst.

[0034] Embodiment 10: The method of Embodiment 9, further comprising combining the deactivated chromium-based catalyst with the copper oxide based heat generating material via a wet impregnation method, wherein the copper oxide based heat generating material includes copper nitrate.

[0035] Embodiment 11: The method of any of Embodiments 9-10, further comprising combining the deactivated chromium-based catalyst with the copper oxide based heat generating material via a solid state method, wherein the copper oxide based heat generating material includes copper oxide.

[0036] Embodiment 12: The method of any of Embodiments 9-11, wherein the metal chromium oxide catalyst includes a copper chromium oxide of the formula $\text{Cu}_x\text{Cr}_y\text{O}_z$, wherein x is 1 to 2, y is 1 to 2, and z is 4 to 5.

[0037] Embodiment 13: The method of any of Embodiments 9-12, wherein the deactivated chromium-based catalyst includes a chromium oxide dehydrogenation catalyst manufactured on an alumina support.

[0038] Embodiment 14: The method of any of Embodiments 9-13, wherein the deactivated chromium-based catalyst includes Cr_2O_3 and Al_2O_3 .

[0039] Embodiment 15: The method of any of Embodiments 9-14, wherein the dried mixture is calcined at a temperature of 300-600 °C, wherein the metal chromium oxide catalyst is CuCrO_4 .

[0040] Embodiment 16: The method of Embodiment 9-15, wherein the dried mixture is calcined at a temperature of 600 °C.

[0041] In general, the invention may alternately comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The invention may additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present invention.

[0042] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other (e.g., ranges of “up to 25 wt.%, or, more specifically, 5 wt.% to 20 wt.%”, is inclusive of the endpoints and all intermediate values of the ranges of “5 wt.% to 25 wt.%,” etc.). “Combination” is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms “first,” “second,” and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from another. The terms “a” and “an” and “the” herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The suffix “(s)” as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term (e.g., the film(s) includes one or more films). Reference throughout the specification to “one embodiment”, “another embodiment”, “an embodiment”, and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments.

[0043] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

CLAIMS

What is claimed is:

1. A method for generating supported metal chromium oxide catalysts, comprising:
 - providing a deactivated chromium-based catalyst;
 - determining the amount of chromium in the deactivated chromium-based catalyst by inductively coupled plasma atomic emission spectroscopy;
 - combining a calculated amount of a metal material with the deactivated chromium-based catalyst to form a mixture, wherein the calculated amount is based on the determined amount of chromium in the deactivated chromium-based catalyst to yield a desired stoichiometry of the metal chromium oxide catalyst;
 - drying the mixture at a temperature of at least 100 °C; and
 - calcining the dried mixture at a temperature of at least 250 °C to form the metal chromium oxide catalysts.
2. The method of Claim 1, further comprising combining the deactivated chromium-based catalyst with the metal material via a wet impregnation method, wherein the metal material includes copper nitrate.
3. The method of any of Claims 1-2, further comprising combining the deactivated chromium-based catalyst with the metal material via a solid state method, wherein the metal material includes copper oxide.
4. The method of any of Claims 1-3, further comprising combining the deactivated chromium-based catalyst with the metal material via a solid state method.
5. The method of any of Claims 1-4, wherein the metal chromium oxide catalyst is a copper chromium oxide of the formula $\text{Cu}_x\text{Cr}_y\text{O}_z$, wherein x is 1 to 2, y is 1 to 2, and z is 4 to 5.
6. The method of any of Claims 1-5, wherein the dried mixture is calcined at a temperature of 600 °C, wherein the metal chromium oxide catalyst is CuCrO_4 .

7. The method of Claim 6, wherein the dried mixture is calcined at a temperature of 600 °C.

8. The method of any of Claims 1-7, wherein a desired stoichiometry of the metal chromium oxide catalyst is a 1:1 molar ratio of metal to chromium.

9. A method for generating a supported metal chromium oxide catalyst, comprising:

combining a deactivated chromium-based catalyst with a copper oxide based heat generating material to form a mixture;

drying the mixture at a temperature of at least 100 °C; and

calcining the dried mixture at a temperature of at least 250 °C to form the supported metal chromium oxide catalyst.

10. The method of Claim 9, further comprising combining the deactivated chromium-based catalyst with the copper oxide based heat generating material via a wet impregnation method, wherein the copper oxide based heat generating material includes copper nitrate.

11. The method of any of Claims 9-10, further comprising combining the deactivated chromium-based catalyst with the copper oxide based heat generating material via a solid state method, wherein the copper oxide based heat generating material includes copper oxide.

12. The method of any of Claims 9-11, wherein the metal chromium oxide catalyst includes a copper chromium oxide of the formula $\text{Cu}_x\text{Cr}_y\text{O}_z$, wherein x is 1 to 2, y is 1 to 2, and z is 4 to 5.

13. The method of any of Claims 9-12, wherein the deactivated chromium-based catalyst includes a chromium oxide dehydrogenation catalyst manufactured on an alumina support.

14. The method of any of Claims 9-13, wherein the deactivated chromium-based catalyst includes Cr_2O_3 and Al_2O_3 .

15. The method of any of Claims 9-14, wherein the dried mixture is calcined at a temperature of 300-600 °C, wherein the metal chromium oxide catalyst is CuCrO_4 .

16. The method of Claim 9-15, wherein the dried mixture is calcined at a temperature of 600 °C.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/053712

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J37/08 B01J23/86 B01J37/02
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)
B01J

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, 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	Acta Cryst ET AL: "INORGANIC COMPOUNDS The Spinel _s CuCr ₂ O ₄ and CuRh ₂ O ₄ ", November, 1 January 1997 (1997-01-01), pages 657-659, XP055406576, Retrieved from the Internet: URL: http://journals.iucr.org/c/issues/1997/06/00/br1169/br1169.pdf Experimental	1-16
X	US 4 861 745 A (HUANG DINAH C [US] ET AL) 29 August 1989 (1989-08-29) column 3, line 44 - line 56 ----- -/-	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

14 September 2017

Date of mailing of the international search report

25/09/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Zieba, Roman

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2017/053712

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHIEN ET AL: "Effect of heat-treatment conditions on Cu?Cr@c-alumina catalyst for carbon monoxide and propene oxidation", APPLIED CATALYSIS A: GENERAL, ELSEVIER, AMSTERDAM, NL, vol. 131, no. 1, 12 October 1995 (1995-10-12), pages 73-87, XP022255260, ISSN: 0926-860X, DOI: 10.1016/0926-860X(95)00136-0 abstract Experimental, 2.1 Catalyst preparation -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2017/053712

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 4861745	A	29-08-1989	EP	0353453 A2		07-02-1990
			IN	172392 B		17-07-1993
			JP	H0275346 A		15-03-1990
			US	4861745 A		29-08-1989
