



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2744576 C 2014/07/08

(11)(21) **2 744 576**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

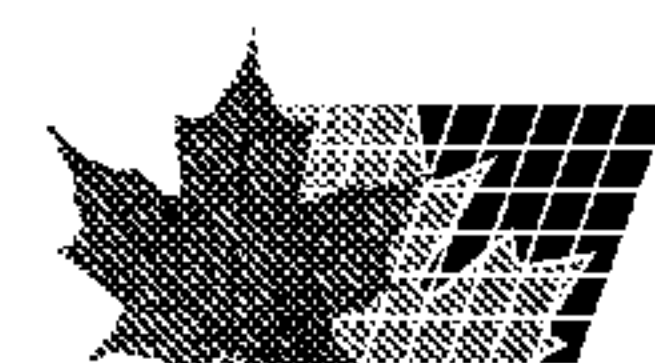
(86) Date de dépôt PCT/PCT Filing Date: 2009/09/21
(87) Date publication PCT/PCT Publication Date: 2010/06/17
(45) Date de délivrance/Issue Date: 2014/07/08
(85) Entrée phase nationale/National Entry: 2011/05/25
(86) N° demande PCT/PCT Application No.: US 2009/057619
(87) N° publication PCT/PCT Publication No.: 2010/068321
(30) Priorité/Priority: 2008/12/11 (US12/332,421)

(51) Cl.Int./Int.Cl. *C01F 7/02* (2006.01),
B22F 9/16 (2006.01)
(72) Inventeur/Inventor:
KANAZIREV, VLADISLAV I., US
(73) Propriétaire/Owner:
UOP LLC, US
(74) Agent: MACRAE & CO.

(54) Titre : PROCEDE DE PRODUCTION D'ALUMINE AMELIOREE
(54) Title: PROCESS FOR PRODUCING ENHANCED ALUMINA

(57) **Abrégé/Abstract:**

The present invention provides an essentially dry method for preparation of enhanced alumina powders. The first step involves rapid calcination of an aluminum compound to produce alumina powder. The alumina powder is mixed with solid ammonium carbonate and a small amount of water. This mixture heats itself although some external heat is helpful to produce am-monium aluminum hydroxycarbonate (dawsonite-type) $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$ upon curing which is then decomposed to produce enhanced alumina having a specific desired morphology and nano-sized dimensions.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
17 June 2010 (17.06.2010)

PCT

(10) International Publication Number
WO 2010/068321 A1

(51) International Patent Classification:

C01F 7/02 (2006.01) *B22F 9/16* (2006.01)

(21) International Application Number:

PCT/US2009/057619

(22) International Filing Date:

21 September 2009 (21.09.2009)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12/332,421 11 December 2008 (11.12.2008) US

(71) **Applicant** (*for all designated States except US*): **UOP LLC** [US/US]; 25 East Algonquin Road, P.O. Box 5017, Des Plaines, Illinois 60017-5017 (US).(72) **Inventor; and**(75) **Inventor/Applicant** (*for US only*): **KANAZIREV, Vladislav I.** [US/US]; UOP LLC, 25 East Algonquin Road, P.O. Box 5017, Des Plaines, Illinois 60017-5017 (US).(74) **Common Representative**: **UOP LLC**; 25 East Algonquin Road, P.O. Box 5017, Des Plaines, Illinois 60017-5017 (US).(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, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (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, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).**Published:**

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title**: PROCESS FOR PRODUCING ENHANCED ALUMINA(57) **Abstract**: The present invention provides an essentially dry method for preparation of enhanced alumina powders. The first step involves rapid calcination of an aluminum compound to produce alumina powder. The alumina powder is mixed with solid ammonium carbonate and a small amount of water. This mixture heats itself although some external heat is helpful to produce ammonium aluminum hydroxycarbonate (dawsonite-type) $\text{NH}_4\text{AlCO}_3(\text{OH})_2$ upon curing which is then decomposed to produce enhanced alumina having a specific desired morphology and nano-sized dimensions.

WO 2010/068321 A1

PROCESS FOR PRODUCING ENHANCED ALUMINA

BACKGROUND OF THE INVENTION

[0001] Alumina powders are widely used in many areas of industry and life such as for supports of catalysts, adsorbents, additives, in the ceramic industry, fillers and others.

5 [0002] There is a need for alumina supports with high BET surface area and pore volume combined with a suitable bulk density, stability and ability easily to accommodate additives. One can refer to such alumina supports as enhanced alumina (EA). Simple alumina powder manufacturing methods are also needed.

10 [0003] Dawsonite, sodium aluminum dihydroxide carbonate ($\text{NaAl(OH)}_2\text{CO}_3$) and its alkali metal and ammonium analogs are useful compounds that either occur naturally or are synthesized by a variety of processes which in the prior art have taken place in aqueous medium. In US 4,356,157, dawsonite was produced by combination of aluminum hydroxide and an alkali metal or ammonium hydrogencarbonate at high pressure and at temperatures between 150° and 250°C.

15 SUMMARY OF THE INVENTION

[0004] This invention provides an essentially dry method for preparation of enhanced alumina powders. It includes three important steps. The first step involves rapid (flash) calcination of an aluminum compound, usually a hydroxide and typically Al(OH)_3 (gibbsite) as conventionally produced in the Bayer process. This step is practiced industrially for manufacturing activated alumina particulates and special powders capable of rehydration. Alumina powder produced in the first step is mixed with solid ammonium carbonate in a blender upon addition of a small amount of water. Ammonium hydrogencarbonate (bicarbonate) NH_4HCO_3 is the preferred carbonate, but other ammonium carbonates such as $(\text{NH}_4)_2\text{CO}_3$, ammonium sesqui carbonate or carbamate can be also used. The mixture heats itself up without addition of external heat, but a moderate heating and curing can be applied to facilitate a reaction that results in the preparation of ammonium aluminum hydroxycarbonate (dawsonite-type) $\text{NH}_4\text{AlCO}_3(\text{OH})_2$. The third step involves the decomposition of ammonium aluminum hydroxycarbonate to obtain enhanced alumina (EA) with specific morphology and the features of a nano-sized material. Carbon dioxide (CO_2) and ammonia (NH_3) and water are gaseous decomposition products of hydroxycarbonate as well

20
25
30

[0005] Carbon dioxide and ammonia can be recovered and reused for the preparation of ammonium bicarbonate that is used as a raw material. The invention differs from the known methods for alumina powder production such as hydrolysis of aluminum alkoxides and different precipitation routes. It differs also from the methods that employ rehydration of flash calcined alumina (FCA) that usually are followed by autoclaving and thermal treatment. No significant liquids or emissions are involved. The carbonate additive can be used in a dry form and can be easily recovered for re-use by capturing NH_3 and CO_2 evolved in the decomposition stage.

[0006] FCA alumina powder produced industrially by flash calcination of gibbsite and known as A-300 product of UOP LLC is mixed in a blender with reagent grade ammonium bicarbonate powder upon addition of small amounts of water. The mixture is free flowing but it changes somewhat the flow pattern and the resistance to mixing upon water addition. The temperature also increases and exceeds 45° to 50°C . After 30 to 45 minutes, the resulting powder is transferred to a plastic container and additionally cured in an oven at 55° to 60°C to complete the reaction. The last step of the process is the thermal decomposition of NH_4 – dawsonite producing enhanced alumina with high BET surface area and pore volume.

[0007] Optionally, the source alumina may undergo a treatment with acid solution followed by washing and drying. The purpose of this treatment being to reduce the residual sodium in the case when the source alumina is derived from the Bayer process of alumina production. Such alumina material normally contains 0.2 to 0.5 mass-% sodium expressed as the oxide. Low soda alumina is desired when used as catalyst support. Instead on the source alumina, the treatment with the acid solution can be performed directly on the enhanced alumina produced after decomposition of the hydroxycarbonate product.

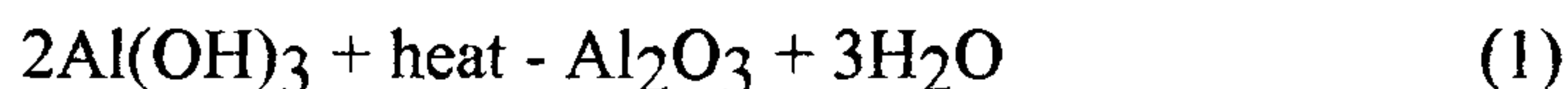
[0007.1] According to one aspect of the present invention there is provided a process for producing alumina comprising a) providing a quantity of alumina powder; b) mixing the alumina powder with a solid ammonium carbonate and from 5 to 30 weight percent water to form a mixture; c) allowing the mixture to cure at a temperature from about 45° to 85°C . to produce ammonium aluminum hydroxycarbonate; and d) then decomposing the ammonium aluminum hydroxycarbonate at a temperature from about 130° to 320°C . to produce an enhanced alumina.

[0008] The process of producing enhanced alumina through described hydroxycarbonate, (dawsonite-type) intermediate can be combined with the use of additives in order to enhance even further the properties of the final product. Additives in both solid and liquid form can be used. Alumina having increased thermal stability is produced if the water in the
5 hydroxycarbonate formation step is replaced by colloidal silica solution.

DETAILED DESCRIPTION OF THE INVENTION

[0009] This invention provides an essentially dry method for preparation of enhanced alumina powders. It includes three important steps. The first step involves rapid (flash)

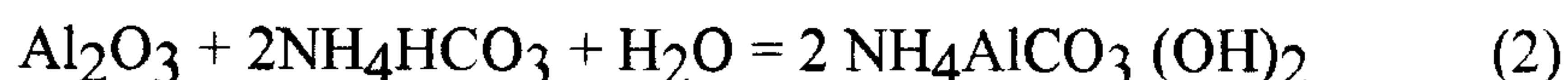
calcination of an aluminum compound, usually a hydroxide and typically $\text{Al}(\text{OH})_3$ (gibbsite) as conventionally produced in the Bayer process. This step is practiced industrially for manufacturing activated alumina particulates and special powders capable of rehydration. The simplified reaction is shown in reaction (1). The alumina produced in the first step is referred to as flash-calcined alumina (FCA).



Other aluminas such as those produced by hydrolysis of aluminum alkoxides, precipitation or hydrothermal treatment of alumina sources can be easily used as a raw material for producing enhanced alumina according the invention provided these aluminas have sufficient reactivity towards ammonium carbonate reagent. Generally, having at least $50 \text{ m}^2/\text{g}$ BET surface area and some rehydratability are important conditions for suitability to serve as alumina raw material.

[0010] Alumina powder produced in the first step is mixed with solid ammonium carbonate in a blender upon addition of a small amount of water. Ammonium bicarbonate carbonate NH_4HCO_3 is the preferred carbonate, but other ammonium carbonates such as $(\text{NH}_4)_2\text{CO}_3$ and sesqui carbonate or carbamate can be also used. The mixture heats itself up without addition of external heat, but a moderate heating and curing can be applied to facilitate reaction (2) that results in the preparation of ammonium aluminum hydroxycarbonate (dawsonite-type) $\text{NH}_4\text{AlCO}_3(\text{OH})_2$ intermediate. Depending on the conditions of the reaction and curing steps, two different hydroxycarbonate intermediates have been identified.

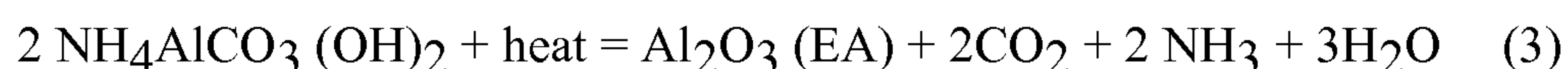
[0011] Curing at longer time and higher temperatures produces the classical ammonium dawsonite as identified by X-ray diffraction patterns while lower temperatures and shorter contact times produces another, yet unknown ammonium aluminum hydroxycarbonate which for the purpose of this invention is named "HYCARB". Both X-ray pattern and FTIR (fourier transform infrared) spectra show significant differences between HYCARB and the classical ammonium dawsonite.



The reaction (2) can be carried in different extend depending on the needs of obtaining enhanced alumina properties. Both partial and practically full conversion of the source alumina to enhanced alumina can be achieved. Repeating step 2 upon addition of fresh

portions of ammonium carbonate speeds up the conversion process of alumina. The use of a small amount, typically from 2 to 10 mass-%, of ammonium aluminum hydroxycarbonate powder in step 2 also facilitates the conversion of the source alumina to hydroxycarbonate

[0012] The third step involves the decomposition of ammonium dawsonite to obtain enhanced alumina (EA) with specific morphology and the features of a nano-sized material – reaction (3).



The decomposition step can be carried out in a variety of devices. Preferred are devices that allow for re-use of the decomposition products. Usually, temperatures from 130° to 320°C are sufficient to fully decompose the hydroxycarbonate intermediate while the lower range is especially preferred when step 2 of the process leads to HYCARB formation. Additional heat treatment can be carried out depending on the application needs. Treatment at temperatures of 600°C is performed if the final product should have gamma alumina as the main alumina crystalline phase.

[0013] The particle morphology of the final alumina differs significantly from that of the source material. The main difference is the appearance of multitude of rod-like subparticles which arise and are entrenched in the original particle. The width of the rods is regularly less than 100 nanometers while the length is limited to few micrometers.

[0014] Carbon dioxide and ammonia can be recovered from reaction (3) and reused for the preparation of ammonium bicarbonate that is used as a raw material for reaction (2). The invention differs from the known methods for alumina powder production such as hydrolysis of aluminum alkoxides and different precipitation routes. It differs also from the methods that employ rehydration of flash calcined alumina (FCA) followed usually by combination of acid treatment, autoclaving and thermal treatment. No significant liquids or emissions are involved. The carbonate additive can be used in a dry form and can be easily recovered for re-use by capturing NH_3 and CO_2 evolved in the decomposition stage.

EXAMPLE 1

[0015] 100g A-300 alumina is mixed with 150g solid ammonium carbonate in a blender upon addition of 24.5g water as described above. The material was cured overnight at 71°C

in a sealed container. The resulting powder is then calcined at 400°C for 1 hour in a muffle oven to produce enhanced alumina with improved thermal stability.

EXAMPLE 2

[0016] The experiment in Example 1 is repeated but 34.5g colloidal silica Nalco™ 1130 is used instead of water.

EXAMPLE 3

[0017] Comparison A-300 powder has been treated at the equipment described in Example 1. No bicarbonate was added but only 30.4 g deionized water. The sample was then calcined at 400°C for 1 hour.

EXAMPLE 4

[0018] The conditions of Example 1 were applied but the duration of 400°C calcination step was 16 hours.

EXAMPLE 5

[0019] The same condition as Example 4 but the calcination temperature was 600°C.

EXAMPLE 6

[0020] The same condition as Example 4 but the calcination temperature was 800°C.

[0021] The calcined samples of Examples 1 to 6 were analyzed using the common method for BET surface area and pore volume determination by low temperature nitrogen adsorption. In addition, selected samples were analyzed for thermal stability using a DTA (differential thermal analyzer), air flow and a temperature programming rate of 5°C/min. The temperature of the specific exothermic effect showing the transition to alpha alumina phase was registered as a measure of thermostability. The data obtained are summarized in the Table whereas the sample according Example 3 represents a comparison sample produced without any addition of ammonium carbonate.

TABLE

Sample	Calcination °C	Calcination hours	BET m ² /g	Pore volume cc/g	Alpha transition temperature by DTA °C
Example 3	400	1	340	0.279	1180
Example 1	400	1	502	0.774	1263
Example 2	400	1	387	0.786	1220
Example 4	400	16	467	0.799	
Example 5	600	16	255	0.712	
Example 6	800	16	169	0.640	

[0022] The data in the Table show that the invention produces alumina with much higher BET surface area, pore volume and thermal stability as compared to the source alumina

WHAT IS CLAIMED IS:

1. A process for producing alumina comprising:

a) providing a quantity of alumina powder;

b) mixing said alumina powder with a solid ammonium carbonate and from 5 to 30
5 weight percent water to form a mixture;

c) allowing said mixture to cure at a temperature from about 45° to 85° C. to produce ammonium aluminum hydroxycarbonate; and

d) then decomposing said ammonium aluminum hydroxycarbonate at a temperature from about 130° to 320° C. to produce an enhanced alumina.

10

2. The process of claim 1 wherein after said mixture has cured an additional amount of said solid ammonium carbonate is added to said ammonium aluminum hydroxycarbonate and allowed to cure at 45° to 85° C.

15

3. The process of claim 1 wherein said alumina powder is selected from the group consisting of calcined $\text{Al}(\text{OH})_3$, alumina produced by hydrolysis of aluminum alkoxide, precipitated alumina and hydrothermally treated alumina.

20

4. The process of claim 1 wherein said alumina powder has a BET surface area greater than 50 m^2/g .

5. The process of claim 1 wherein said mixture is allowed to cure without application of heat to said mixture.

25

6. The process of claim 1 wherein heat is applied to said mixture in addition to heat produced by an exothermic reaction from said mixture.

7. The process of claim 1 wherein said ammonium carbonates are ammonium bicarbonate, ammonium carbonate, ammonium carbamate or ammonium sesqui carbonate.

30

8. The process of claim 1 wherein said ammonium carbonate comprises about 2 to 10 mass-% ammonium aluminum hydroxycarbonate.

9. The process of claim 1 wherein carbon dioxide and ammonia produced from said decomposition of said ammonium aluminum hydroxycarbonate are combined to produce a bicarbonate that comprises at least a portion of said solid ammonium carbonate.

5

10. The process of claim 1 wherein said enhanced alumina is additionally treated with acid solutions to remove the residual sodium contained in source alumina.