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(54) Title: IMPROVED MECHANICAL STRENGTH OF HYDROTALCITE-BASED OXIDES

(57) Abstract: A hydrotalcite-based material having an improved mechanical strength, said hydrotalcite having the following general formula: $M^{2+}_aM^{3+}_b(OH)_e(A^{n-})_d{}^*xH_2O$ wherein M^{2+} is at least one divalent metal; M^{3+} is at least one trivalent metal; A is an n-valent anion, n is 1 or 2 and a and b are positive numbers, a > b, which hydrotalcite is deposited on alumina or an alumina precursor, a process of preparing said hydrotalcite-based material, the use thereof as a catalyst support material, a catalyst for the dehydrogenation of propane, and a process using such a catalyst in the dehydrogenation of propane.

ACAT-1440. Theta-alumina (Puralox Nwa-85, 23.0 g, 0.23 mol) was suspended in distilled water (200 ml) and heated to 60°C. Two solutions were prepared; one with $Mg(NO_3)_2.6H_2O$ (233 g, 0.91 mol) and $Al(NO_3)_3.9H_2O$ (34.0 g, 0.09 mol) in distilled water (900 ml), and another with Na_2CO_3 (4.8 g, 0.045 mol) and NaOH (45.2 g, 1.1 mol) in distilled water (900 ml). The two solutions were dripped into the aqueous suspension of theta-alumina (duration 45 min). The pH in the precipitate solution was 9.5-10. The precipitate was filtered, then washed to neutrality and left overnight.

$SnCl_2.2H_2O$ (0.4804 g, 2.13 mmol) was dissolved in conc. HCl (10 ml). $H_2PtCl_6.6H_2O$ (0.158 g, 0.38 mmol) was dissolved in distilled water (50 ml), and the tin chloride solution added. The resulting solution had a red colour.

The precipitate was suspended in distilled water (400 ml) and the Pt-Sn solution dripped into the suspension, which had a neutral pH value. The suspension was stirred for 45 min., then filtered and washed twice with distilled water. The product was then dried at 100°C/16 h. Calcination of the product was performed at 800°C/15 hours, yielding a BET area of 91 m^2/g. After pelletisation, the BET area dropped to 77 m^2/g.

The X-Ray diffraction pattern of the final material indicated a strong interaction between the suspended alumina and the solution: When the alumina particles were crushed and sieved to a particle size < 90 micron prior to suspension, then only the hydrotalcite phase (and no alumina phase) was visible by XRD in the final catalyst. With larger or mixed particle sizes, both the hydrotalcite and alumina phases were visible by XRD after the precipitation step. The catalyst used in the further study (Example 5 below) is the one with small alumina particles (<90 micron).

Example 3. Comparative Example A.

C440-104. An Mg-Al hydrotalcite was prepared according to Example 1, but without a suspended binder material. After precipitation, the material was impregnated with Pt

and Sn, then dried and calcined at 800°C/15 hours. The BET area of the calcined product was 145 m^2/g.

Example 4. Comparative Example B.

ACAT-1443. A material was prepared according to a procedure described in GB 2 311 790 (to British Gas), but with some modifications in the precipitate composition (e.g. Mg was used as a cation instead of Ni).

Three aqueous mixtures were prepared:

Solution A: $Mg(NO_3)_2.6H_2O$ (116.5 g, 0.45 mol) and $Al(NO_3)_3.9H_2O$ (17.0 g, 0.045 mol) in distilled water (500 ml).

Solution B: Na_2CO_3 (78.4 g, 0.74 mol) in distilled water (500 ml).

Suspension C: Kaolin (2.62 g) and MgO (1.24 g, 0.03 mol) in distilled water (30 ml).

Solutions A and B were heated to 75°C. Solution B was dripped into solution A under stirring (duration: 30 min). The pH in the precipitate solution was 10. Suspension C was added and the final mixture stirred for some minutes. The product was filtered and then washed several times with distilled water.

$SnCl_2.2H_2O$ (0.240 g, 1.06 mmol) was dissolved in conc. HCl (10 ml). $H_2PtCl_6.6H_2O$ (0.078 g, 0.19 mmol) was dissolved in distilled water (50 ml), and the tin chloride solution added. The resulting solution had a red colour.

The precipitate was suspended in distilled water (200 ml) and the Pt-Sn solution dripped into the suspension, which had a neutral pH value. The suspension was stirred for 45 min., then filtered and washed twice with distilled water. The product was then dried at 100°C/16 h and calcined at 450°C/5 hours. The product was then crushed and dry mixed with Secar 71 (Lafarge, 7.2 g) (a mixture of CaO and Alumina) and 2wt% graphite, and then stirred for 1 h. The product was pelleted, steamed at 240°C/16h and soaked in distilled water (16 h). The soaking procedure led to pellet cracking. Subsequently, the pellets were dipped in a 2% KOH aqueous solution. The pellets were crushed and the material pelleted once more. XRD of the product showed the presence of a crystalline hydrotalcite phase, as well as MgO and Secar-71

($Ca_3Al_{10}O_{18}$). The BET area of the product was 30 m^2/g, which is within the expected range for uncalcined hydrotalcites. XRD of the same product after use as a PDH catalyst (Example 5) indicated that the hydrotalcite phase is converted to Mg(Al)O during use as a PDH catalyst.

Example 5. Propane dehydrogenation (PDH) tests

The materials prepared according to Examples 1-4 were subjected to testing under PDH conditions at 600°C in a quartz reactor with i.d. 23 mm. The reactor was heated to 600°C in a N_2 flow, then subjected to reduction, PDH and regeneration test cycles according to Table 1. The GHSV was 1000 h^{-1} based on propane. The test was stopped after 6 test cycles with regeneration, and the catalyst cooled to room temperature in a N_2 flow. GC analysis of the reactor effluent showed the presence of both propane and propene from all catalysts.

Table 1. PDH test conditions.

	Step 1 Reduction	Step 2 PDH	Step 3 1% O_2	Step 4 5% O_2	Step 5 10% O_2	Step 6 20%O_2
N_2 (ml/min)	241		277	218	146	
Air (ml/min)			14.3	73	146	291
Propane (ml/min)		92.9				
H_2O (g/h)		8.3				
H_2 (ml/min)	50	13.1				
Duration (min)	30	1200	60	60	60	60

Visual inspection of the tested pellets showed no sign of damage for the samples prepared according to Examples 1, 2 and 4. However, some fine powder had been formed from the sample prepared without binder (Example 3) during testing. Judging from the remaining pellets, this powder originated from the edges of each pellet. None of the pellets were cracked.

Example 6. Mechanical strength of pellets

The materials which had been prepared according to Examples 1-4, and tested according to Example 5, were subjected to mechanical strength measurements by using a Side Crushing Strength procedure (SCS). The SCS raw data for each material are shown in Figure 2. As can be seen, the mechanical strength measured for different pellets of one catalyst varies significantly. However, when calculating the average SCS value for each catalyst, as shown in Table 2, some trends are observed:

- The catalysts that are precipitated on suspended pseudo-boehmite and theta-alumina (Examples 1 and 2) have significantly higher SCS values than the sample prepared without binder (Example 3).
- Alumina and pseudo-boehmite give materials with similar mechanical strength before and after testing.
- The catalyst prepared using the modified BG recepy (Example 4) has a similar mechanical strength to the sample prepared without binder (Example 3).
- The mechanical strength decreases during PDH testing for all samples, especially for the samples with the highest initial SCS value. However, even after 1 week of testing, the SCS value of the strongest sample (Example 1) is 74% higher than for the sample prepared without binder (Example 3).
- The mechanical strength of the final material seems to be uninfluenced by whether or not the crystallinity of the alumina (precursor) is maintained throughout the precipitation and metal deposition steps.

Table 2. Average SCS values for the materials in Examples 1-4 before and after testing as PDH catalysts for 1 week.

Catalyst	SCS before testing (N)	SCS after PDH testing (N)
1 (ACAT-1439)	436	238
2 (ACAT-1440)	441	224
3 (C440-104)	174	137
4 (ACAT-1443)	196	100

Example 7. Addition of alumina after precipitation and calcination of the hydrotalcite.

A Mg-Al catalyst was prepared according to Example 1, but without a suspended material in the precipitation vessel. After completing the precipitation and metal addition steps, the hydrotalcite material was dried at 100°C/16 hours, and then dry mixed with pseudo-boehmite (AlO(OH), Vista B, 22.98 g, 0.38 mol). The mixture was then calcined at 800°C/15 hours, and subsequently pelleted and subjected to SCS measurements.

The average SCS value of the calcined material was ---- N. This result shows that dry mixing the calcined hydrotalcite with alumina significantly enhances the mechanical strength of the final material compared to calcined hydrotalcite alone. However, the mechanical strength of this material is clearly inferior to the mechanical strength obtained by preparing the hydrotalcite in a suspension of hydrotalcite (Example 1).

Example 8. Alumina addition after precipitation of the hydrotalcite

A catalyst was prepared according to Example 1, but without a suspended material in the precipitation vessel. After the precipitation and metal deposition steps, but before drying, pseudo-boehmite (AlO(OH), Vista B, 22.98 g, 0.38 mol) was added to the precipitate. The final material was subjected to drying (100°C/16 hours), calcination (800°C/15 hours), pelletisation and SCS measurements. The average SCS value of the pellets was --- N.

This result shows that adding the alumina precursor after precipitation of the hydrotalcite, but before drying, leads to a material with a similar mechanical strength to the material where the alumina precursor is added before precipitation. A comparison between Example 7 and Example 8 indicates that it is advantageous to add the alumina (precursor) before drying the hydrotalcite.

Example 9. Preparation of hydrotalcite in a lower quantity of suspended pseudo-boehmite

A material was prepared according to Example 1, with the only exception that a lower amount of pseudo-boehmite (AlO(OH), Vista B, 4.60 g, 0.076 mol) was used. The average SCS value of the final material was --- N. This result shows that a material with a high mechanical strength may be obtained by the suspension – precipitation method, even when the amount of alumina in the final material is quite low.

Conclusion

The Examples above clearly illustrate that the presence of an alumina or alumina precursor support in a hydrotalcite-based oxide material, i. e. the hydrotalcite-based oxide material is deposited on said alumina or alumina precursor support, uexpectedly leads to an enhanced mechanical strength both initially and after PDH testing. The use of alumina itself, or of a hydrated form of alumina, give similar results. The PDH tests should be considered as a tool to illustrate that the materials can withstand quite severe conditions, i.e. cycling between coking, steam-rich conditions and oxidizing conditions, all at ca. 600°C.

Further, the Examples illustrate that the addition of the alumina (precursor) as a liquid suspension before precipitation of the hydrotalcite, or directly after the precipitation step, is particularly advantageous.

Finally, the Examples illustrate that a silica-based binder described in the literature[5] gives only a slight improvement of the mechanical strength of the materials used here, compared to a similar material with no binder.

In conclusion, the Examples illustrate that the binder composition, as well as the method of binder addition, are both of major importance for the mechanical strength of hydrotalcite-based materials.

It is to be expected that this result is not restricted to the hydrotalcite preparation method used in the Examples, but is also achievable for other hydrotalcite preparation methods. It is further expected that the results are valid also for an uncalcined hydrotalcite-like material.

These results were not to be expected in view of the prior art known to the applicant on the filing date of the instant application.

The examples presented above must in now way be construed as a limitation of the present invention, but merely as illustrations thereof, the scope of the invention being fully defined in the appending claims.

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Improved mechanical strength of hydrotalcite-based oxides

FIELD OF INVENTION

The present invention relates to hydrotalcites. Particularly the invention relates to calcined hydrotalcites having an enhanced mechanical strength. The invention further relates to the processes of preparing such materials. The invention also relates to the use of such materials as catalyst carriers in catalytic processes, particularly for the dehydrogenation of paraffins. Further the invention relates to processes of preparing alkenes by the use of such dehydrogenation catalysts.

BACKGROUND OF INVENTION

Mixed $M^{2+}(M^{3+})O$ materials may be obtained by calcination of a hydrotalcite-like material (HT) of general formula:

$$M^{2+}_aM^{3+}_b(OH)_c(A^{n-})_d*xH_2O$$

wherein M^{2+} is at least one divalent metal; M^{3+} is at least one trivalent metal; A is an n-valent anion, n is 1 or 2 and a and b are positive numbers, a > b.

Several methods for the preparation of hydrotalcites are known from the literature:

The most common method consists in mixing a solution containing the metal salts with a basic solution, resulting in rapid precipitation of the hydrotalcite. The two aqueous solutions may either be added slowly into a third vessel where the precipitate solution holds a constant pH[1], or the metal salt solution may be added into the basic solution at varying pH. In the latter case, the precipitate is left to crystallize in the liquid after the mixing step has been completed[2].

In a second method, pseudo-boehmite is slurried in water, followed by addition of an organic acid such as acetic acid. Magnesium oxide is then added, and the slurry allowed to react for some hours, thus yielding a product with hydrotalcite structure. This method is described in [3].

In a third method, aluminium metal and magnesium metal are reacted in 1-hexanol, and then hydrolysed by a neutral or basic, aqueous solution, resulting in a gel-like product with a hydrotalcite structure. This method is described in [4].

Mixed oxides derived from hydrotalcites have found wide applications, e.g. as catalysts or catalyst carrier materials, adsorbents, ion exchange materials, etc[5].

The mechanical strength of such materials has been the focus of several studies.
In [6], a material is produced by dry mixing hydrotalcite (20-80%) with activated alumina (80-20%), then optionally rehydrating the mixture and finally activating it at 5-600°C. An alternative approach consists in activating the hydrotalcite at 5-600°C prior to mixing with alumina. The crush strength of the mixed material is significantly higher than for activated hydrotalcite alone. The claims cover any adsorbent or substrate with the said composition and activation treatment.
In [7], a hydraulic cement, containing Ca, Al and Mg or Si, is mixed with aluminium powder and a CO oxidation catalyst under dry or aqueous conditions, followed by hardening at 30-100°C. Hydrotalcite is mentioned as a possible catalyst support material under the invention, but no such examples are included.
In [8], a spray dried hydrotalcite, prepared from AlO(OH), MgO and an organic acid, is mixed with an inorganic material (such as TiO_2, ZnO, $CuCrO_x$, zeolite or celite) and water, then shaped and dried, and optionally calcined at 400-800°C. The resulting materials have a high crush strength compared to the inorganic materials alone. In one example, the influence of the calcination temperature is investigated, and indicates a decrease in the crush strength with an increasing calcination temperature, compared to the uncalcined material.
In [9], a binder, consisting of an Si-Al-O (kaolin or bentonite) material, is added either before or after the precipitation of a Ni-Al-(Cr) hydrotalcite. According to the patent, both methods give materials with (quote): "....(c) excellent strength and retention of this strength in operation; (d) no loss of strength or activity or leaching in steam environments, e.g. silica or potassium leaching." No comparison is made between the two binder addition methods, nor with a material without binder.

In the present work, it has surprisingly been found that the preparation of a hydrotalcite by coprecipitation in a suspension of alumina, Al_2O_3, or an alumina precursor, such as pseudo-boehmite, AlO(OH), leads to a material which has significantly higher mechanical strength than a material where alumina is added after

coprecipitation and drying of the hydrotalcite, and also compared to a material obtained by addition of an Si-Al-O binder.

A procedure similar to the one used here has previously been described for a Ni-Al hydrotalcite-based material[10]. However, the purpose of that study was to decrease the Ni content of the final material, and no reference is made to the mechanical strength of the catalyst.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a hydrotalcite-based material having an improved mechanical strength, said hydrotalcite having the following general formula:

$$M^{2+}_aM^{3+}_b(OH)_c(A^{n-})_d*xH_2O$$

wherein M^{2+} is at least one divalent metal; M^{3+} is at least one trivalent metal; A is an n-valent anion, n is 1 or 2 and a and b are positive numbers, a > b, which hydrotalcite is deposited on alumina or an alumina precursor.

Particularly the hydrotalcite-based material having an improved mechanical strength, said hydrotalcite having the following general formula:

$$M^{2+}_aM^{3+}_b(OH)_c(A^{n-})_d*xH_2O$$

wherein M^{2+} is at least one divalent metal; M^{3+} is at least one trivalent metal; A is an n-valent anion, n is 1 or 2 and a and b are positive numbers, a > b,

said hydrotalcite-based material being prepared by bringing the hydrotalcite in an intimate contact with alumina or an alumina precursor in a liquid suspension.

In the above mentioned material M^{2+} is preferably Mg and M^{3+} is Al.

According to a preferred embodiment thereof the alumina or alumina precursor is added as a liquid suspension.

Further said hydrotalcite is preferably prepared in a liquid suspension of alumina or an alumina precursor.

Particularly the hydrotalcite preparation takes place during simultaneous addition of a suspension of alumina or an alumina precursor.

Preferably the above mentioned liquid is water.

It is further preferred that the hydrotalcite is prepared by a coprecipitation method.

Particularly said hydrotalcite is subsequently dried and calcined at a temperature in the range 400-1300°C, preferably at 500-1000°C.

Still more preferred the calcination preferably takes place at a temperature in the range 600-900°C.

Further the present invention relates to a process for the preparation of a hydrotalcite having an improved mechanical strength, said hydrotalcite having the following general formula:

$$M^{2+}_{a}M^{3+}_{b}(OH)_{c}(A^{n-})_{d}*xH_2O$$

wherein M^{2+} is at least one divalent metal; M^{3+} is at least one trivalent metal; A is an n-valent anion, n is 1 or 2 and a and b are positive numbers, a > b,

said hydrotalcite-based material being prepared by bringing the hydrotalcite in an intimate contact with alumina or an alumina precursor in a liquid suspension.

In this process, particularly M^{2+} is Mg and M^{3+} is Al.

In said process the alumina or alumina precursor is preferably added as a liquid suspension.

In said process said hydrotalcite is particularly prepared in a liquid suspension of alumina or an alumina precursor.

Preferably the hydrotalcite preparation takes place during simultaneous addition of a suspension of alumina or an alumina precursor.

Particularly the above mentioned liquid is water.

In a preferred embodiment of the invention said hydrotalcite is prepared by a coprecipitation method.

According to a preferred embodiment of this process said hydrotalcite is subsequently dried and calcined at a temperature in the range 400-1300°C, preferably at 500-1000°C.

Further according to a preferred embodiment of this process, the calcination takes place at a temperature in the range 600-900°C.

Still another aspect of the present invention involves the use of the hydrotalcite-based material defined and prepared above as a catalyst support material.

Yet a further aspect of this invention comprises a catalyst for use in the dehydrogenation of alkanes, said catalyst comprising a catalytic active metal being impregnated on the hydrotalcite-based material defined and prepared as stated above.

In this catalyst the catalytic active metal is particularly Pt.

Particularly the catalytic active metal Pt is coimpregnated with Sn.

Further the present invention also relates to a process for the catalytic dehydrogenation of propane, wherein propane is contacted with the catalyst defined above at the standard pressure, temperature and space velocity conditions of such dehydrogenation reactions.

At last the present invention relates to the use of the catalyst defined above in the dehydrogenation of propane.

EXAMPLES

The invention is illustrated through the following examples, which must not be construed as limitations to the invention.

General

Characterisation

X-Ray powder diffraction was performed using Cu K_α radiation with a Siemens D5000 2-theta diffractometer. The BET surface area was measured using a

Quantachrome monosorb apparatus. Side crushing strength measurements (SCS) were performed on a Schenck Krebel RM100 universal material test apparatus.

Pelleting procedure

The powder (ca. 1 g) was pressed in an IR tablet press with diameter 13 mm, using a pressure of 120 kg/cm^2, yielding a pellet height of 5 mm.

Example 1. Preparation of hydrotalcite on suspended pseudo-boehmite, and a catalyst supported thereon.

ACAT-1439. Pseudo-boehmite (AlO(OH), Vista B, 22.98 g, 0.38 mol) was suspended in distilled water (200 ml) and heated to 60°C. Two solutions were prepared; one with $Mg(NO_3)_2.6H_2O$ (233 g, 0.91 mol) and $Al(NO_3)_3.9H_2O$ (34.0 g, 0.09 mol) in distilled water (900 ml), and another with Na_2CO_3 (4.8 g, 0.045 mol) and NaOH (45.2 g, 1.1 mol) in distilled water (900 ml). The two solutions were dripped into the aqueous suspension of pseudo-boehmite (duration 45 min). The pH in the precipitate solution was 9.5-10. The precipitate was filtered, then washed to neutrality and left overnight.

$SnCl_2 2H_2O$ (0.4804 g, 2.13 mmol) was dissolved in conc. HCl (10 ml). $H_2PtCl_6 6H_2O$ (0.157 g, 0.38 mmol) was dissolved in distilled water (50 ml), and the tin chloride solution added. The resulting solution had a red colour.

The Mg-Al precipitate was suspended in distilled water (400 ml) and the Pt-Sn solution dripped into the suspension, which had a neutral pH value. The suspension was stirred for 45 min., then filtered and washed twice with distilled water. The product was then dried at 100°C/16 h and subjected to XRD measurements. The XRD pattern clearly showed the presence of both hydrotalcite and pseudo-boehmite (Figure 1). Calcination of the product was performed at 800°C/15 hours, yielding a BET area of 118 m^2/g. After pelletisation, the BET area dropped to 103 m^2/g.

Claims

1. A hydrotalcite-based material having an improved mechanical strength, said hydrotalcite having the following general formula:

$$M^{2+}_aM^{3+}_b(OH)_c(A^{n-})_d*xH_2O$$

wherein M^{2+} is at least one divalent metal; M^{3+} is at least one trivalent metal; A is an n-valent anion, n is 1 or 2 and a and b are positive numbers, a > b, which hydrotalcite is deposited on alumina or an alumina precursor.

2. The hydrotalcite-based material of claim having an improved mechanical strength, said hydrotalcite having the following general formula:

$$M^{2+}_aM^{3+}_b(OH)_c(A^{n-})_d*xH_2O$$

wherein M^{2+} is at least one divalent metal; M^{3+} is at least one trivalent metal; A is an n-valent anion, n is 1 or 2 and a and b are positive numbers, a > b,

said hydrotalcite-based material being prepared by bringing the hydrotalcite in an intimate contact with alumina or an alumina precursor in a liquid suspension.

3. The material according to the claims 1 and 2, wherein M^{2+} is Mg and M^{3+} is Al.

4. The material according to the claims 2 and 3, wherein the alumina or alumina precursor is added as a liquid suspension.

5. The material according to the claims 2-4, said hydrotalcite being prepared in a liquid suspension of alumina or an alumina precursor.

6. The material according to the claims 2-5, wherein hydrotalcite preparation takes place during simultaneous addition of a suspension of alumina or an alumina precursor.

7. The material according to the claims 2-6, wherein the liquid is water.

8. The material according to the claims 2-7, said hydrotalcite being prepared by a coprecipitation method.

9. The material according to any of the claims 2-8, said hydrotalcite being subsequently dried and calcined at a temperature in the range 400-1300°C, preferably at 500-1000°C.

10. The material according to the claim 9, wherein the calcination preferably takes place at a temperature in the range 600-900°C.

11. A method for the preparation of a hydrotalcite of the claims 1 and 2 having an improved mechanical strength, said hydrotalcite having the following general formula:

$$M^{2+}_{a}M^{3+}_{b}(OH)_{c}(A^{n-})_{d}*xH_2O$$

wherein M^{2+} is at least one divalent metal; M^{3+} is at least one trivalent metal; A is an n-valent anion, n is 1 or 2 and a and b are positive numbers, a > b,

said hydrotalcite-based material being prepared by bringing the hydrotalcite in an intimate contact with alumina or an alumina precursor in a liquid suspension.

12. The method of the claim 11, wherein M^{2+} is Mg and M^{3+} is Al.

13. The method of the claim 11 and 12, wherein the alumina or alumina precursor is added as a liquid suspension.

14. The method of the claims 11 - 13, said hydrotalcite being prepared in a liquid suspension of alumina or an alumina precursor.

15. The method of the claims 11- 14, wherein hydrotalcite preparation takes place during simultaneous addition of a suspension of alumina or an alumina precursor.

16. The method of the claims 11 - 15, wherein the liquid is water.

17. The method of the claims 11 - 16, said hydrotalcite being prepared by a coprecipitation method.

18. The method of any of the claims 11 - 17, said hydrotalcite being subsequently dried and calcined at a temperature in the range 400-1300°C, preferably at 500-1000°C.

19. The method of the claim 18, wherein the calcination preferably takes place at a temperature in the range 600-900°C.

20. Use of a hydrotalcite-based material of the the claims 1 – 10 as a catalyst support material.

21. A catalyst for use in the dehydrogenation of alkanes, said catalyst comprising a catalytic active metal being impregnated on the hydrotalcite-based material of the claims 1 – 10 .

22. The catalyst of the claim 21, wherein the catalytic active metal is Pt.

23. The catalyst of the claim 22, wherein the catalytic active metal Pt is coimpregnated with Sn.

24. A process for the catalytic dehydrogenation of propane, wherein propane is contacted with the catalyst of the claims 21 – 23 at the standard pressure, temperature and space velocity conditions for such dehydrogenation reactions.

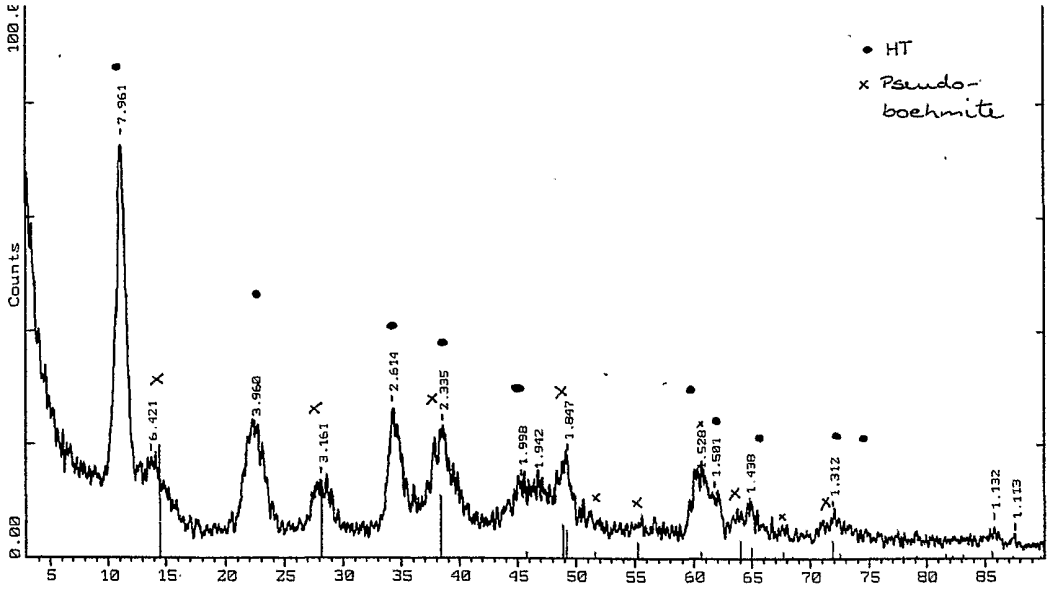

Figure 1. XRD pattern of hydrotalcite (HT) prepared on suspended pseudo-boehmite and subsequently dried at 100°C (Example 1).

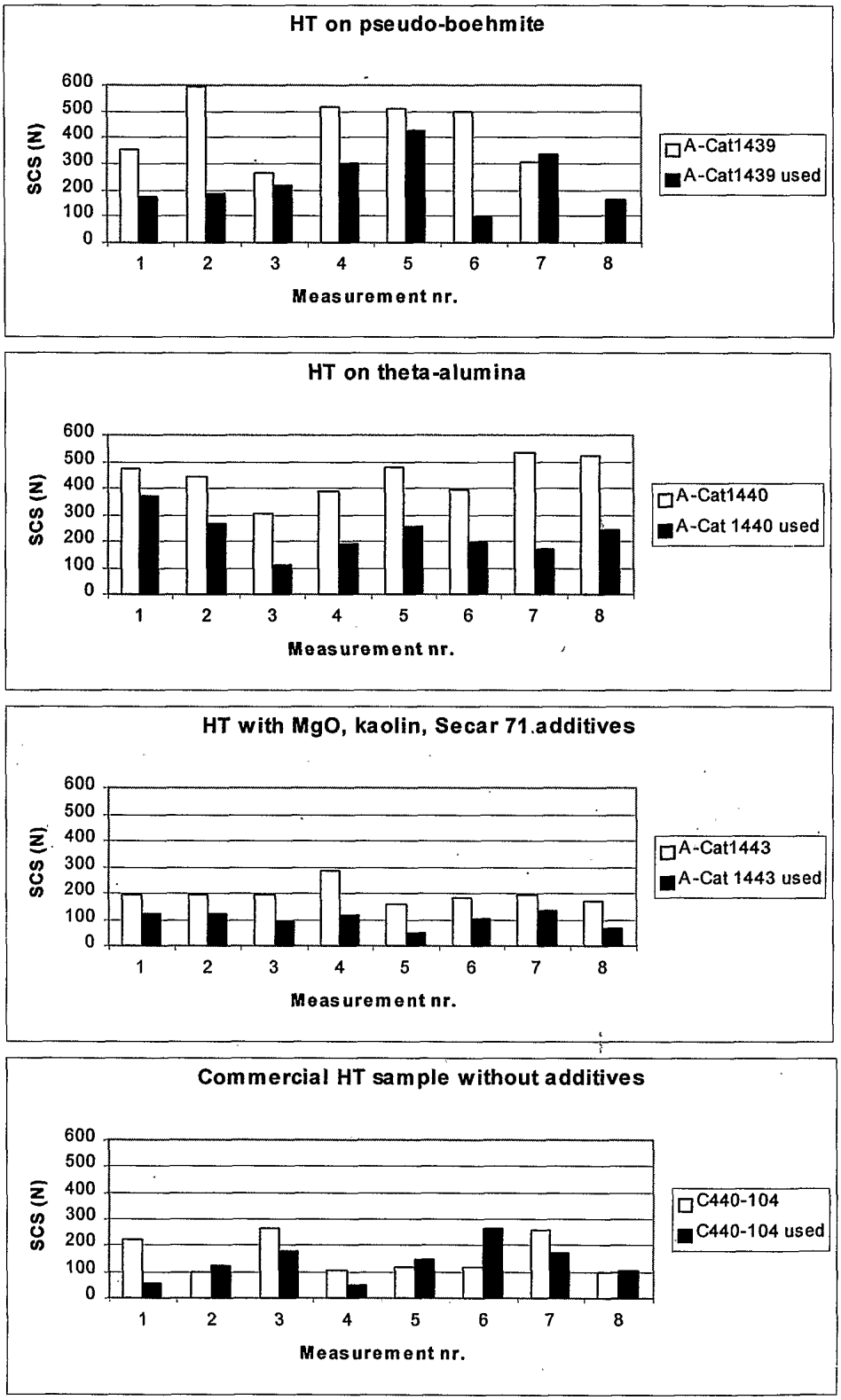

Figure 2. Side Crushing Strength values of calcined and PDH tested materials. "ACAT-1439" = Example 1, "ACAT-1440" = Example 2, "ACAT-1443" = Example 4, "C440-104" = Example 3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 01/00196

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C01F 7/00
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)

IPC7: C01F

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

SE,DK,FI,NO classes as above

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4656156 A (CHANAKYA MISRA), 7 April 1987 (07.04.87), column 4, line 11 - line 25; column 4, line 35 - line 47	1,2,20
X	US 5039645 A (DAVID J. ELLIOTT ET AL), 13 August 1991 (13.08.91), column 2, line 20 - line 36	1,3,20

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

* Special categories of cited documents:
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"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 Sept 2001	10 -09- 2001
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Bengt Christensson/MP Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

(08/01

International application No.
PCT/NO 01/00196

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4656156 A	07/04/87	NONE	
US 5039645 A	13/08/91	NONE	