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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 January 2020 (23.01.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/016902 A1

(51) International Patent Classification:
C07C 13/15 (2006.01) *C07C 5/05* (2006.01)
C07C 13/23 (2006.01) *B01J 25/02* (2006.01)
C07C 23/263 (2006.01)

(21) International Application Number:
PCT/IN2018/050597

(22) International Filing Date:
14 September 2018 (14.09.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
201831027252 20 July 2018 (20.07.2018) IN

(71) Applicant: **HALDIA PETROCHEMICALS LIMITED** [IN/IN]; Tower 1, Bengal Eco Intelligent Park (Techna), Block EM, Plot No 3, Sector V, Salt Lake, PO: Bidhan Nagar, District: North 24 Paraganas, Kolkata 700091 (IN).

(72) Inventors: **SENSARMA, Soumen**; C3-62 Elite Empire, Balewadi, Pune 411045, Maharashtra, Pune 411045 (IN). **DATTA, Raj Kumar**; 656/1, SaratChatterjee Road, Shibpur, Howrah 711102, West Bengal (IN). **KUNDU, Sandip**; 30/B, East Hospital Road, 368 Kalikapur, Kolkata 700068, West Bengal (IN). **ADHIKARY, Koushik**; Vill-Uttarpirpur, P.o- Baniban, P.S- Uluberia, Dist-Howrah 711316, West Bengal (IN). **GHOSH, Ranajit**; c/o- Rajendra Kumar Ghosh Fatakdwar Para, P.O.+P.S.- Kalna, Dist.- Burdwan 713409, West Bengal (IN). **BISWAS, Atanu**; Lakshminathpur, Baduria, (N)-24-Parganas, West Bengal 743401 (IN).

(74) Agent: **KHAITAN & CO**; One Indiabulls Centre, 13th Flr,841Senapati Bapat Marg, Mumbai 400013 (IN).

(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))*
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

WO 2020/016902 A1

(54) Title: SELECTIVE HYDROGENATION OF CYCLIC DIENE TO CORRESPONDING CYCLIC MONO OLEFIN USING SONICATED RANEY NICKEL

(57) Abstract: The present invention provides an improved and economical process for selective hydrogenation of cyclic di-olefins to their corresponding cyclic mono-olefins, essentially in presence of sonicated S1-modified Raney-Nickel as a highly active hydrogenation catalyst.

Title of the invention

SELECTIVE HYDROGENATION OF CYCLIC DIENE TO CORRESPONDING CYCLIC MONO OLEFIN USING SONICATED RANEY NICKEL

FIELD OF THE INVENTION

The present invention relates to the field of chemical technology. More particularly, the present invention relates to an improved and economical process for selective production of cyclic mono-olefins from their corresponding cyclic di-olefins, in presence of sonicated Raney-Nickel catalyst.

BACKGROUND AND PRIOR ART OF THE INVENTION

At the present time, cyclic olefins, specifically cyclic di-olefins like cyclopentadiene, 1, 5-cyclooctadiene, cyclohexadiene etc. play a major role in field of chemical and/or polymer technology. These cyclic di-olefins are often obtained in excess amounts as by-products during petroleum cracking and hence considerable interest lies among the industries or researchers in converting them to value-added products for better utilization.

Cyclopentadiene is produced in bulk amounts as by-products from steam cracking of naphtha during production of ethylene primarily. Its mono-olefinic form that is cyclopentene has been found to be useful as a monomer for the formation of general purpose elastomers by ring opening polymerization of cyclopentene. Cyclopentene as a monomer is also extensively used for synthesis of plastics, and in a number of chemical syntheses such as preparation of hydrocarbons (e.g. cyclopentane), halogenated hydrocarbons (e.g. chlorocyclopentene), high valued ketones (e.g. cyclopentanone), high value alcohol (e.g. cyclopentanol) and many more. It is further useful for preparation of different aroma products. Additionally, cyclopentadiene is an easily produced, readily available and inexpensive material of quite limited usefulness in the

field of organic synthesis, while cyclopentene is a comparatively expensive material which is not readily available and which is difficult and costly to prepare. Likewise, 1, 5-cyclooctadiene is obtained while dimerization of butadiene which is a cracked product of C-4 hydrocarbon butane. Its mono-olefinic form that is cyclooctene is a preferred intermediate for synthesis of suberic acid and omega-aminooctanoic acid, a nylon-8 precursor. Similarly, mono-olefinic form of cyclohexadiene which is cyclohexene is useful in a diverse range of chemical synthesis and for industrial and consumer uses like waterproof coatings, crack resistant films, elastomers, adhesives, precursor to the epoxide, diol and other useful downstream products. Therefore, it is always advantageous to convert portions of cyclopentadiene and/or cyclooctadiene and/or cyclohexadiene produced in excess amounts in industries as by product into their more valuable mono-olefinic forms like cyclopentene, cyclooctene and/or cyclohexene respectively. The same can be achieved by means of a hydrogenation reaction that can selectively convert these cyclic di-olefins to their corresponding cyclic mono-olefinic forms.

Few prior arts have reported such hydrogenation of cyclopentadiene to cyclopentene:

For instance, in US patent no. 2360555, issued on October 17, 1944 discloses a selective hydrogenation of one of the two conjugated double bonds of a cyclic diolefin to produce the corresponding cyclic monoolefin which is accomplished by conducting the hydrogenation in the liquid phase in the presence of an active hydrogenation catalyst, under moderate hydrogen pressure, such as 2 to 5 atmospheres absolute (29.4 to 73.5 psig), and at temperature 0 to 40 °C and up to 100 °C, using pyrophoric nickel metal catalyst, such as Raney nickel.

US patent no. 3857894, issued on December 31, 1974, discloses hydrogenation of cyclopentadiene to cyclopentene in the presence of a palladium catalyst and a small amount of an aqueous solution of zinc salt having a water/zinc ratio of at least 1/1 by weight.

US patent no. 3819734, issued on July 25, 1974, relates to hydrogenation of cyclopentadiene to cyclopentene by bringing cyclopentadiene into contact with a catalyst consisting essentially of (1) nickel, on a magnesium or zinc oxalate support, (2) a ligand selected from the group consisting of trimethyl phosphine, triethyl phosphine, methyl ethyl propyl phosphine, trimethylphosphite, triethylphosphite, tributylphosphite, triphenylphosphite, etc., while in the presence of hydrogen, at temperatures from 0 °C and at pressures from 0 to 1000 pounds per square inch gauge.

US patent no. 3994986, issued on Nov. 30, 1976, discloses a process for preparation of cyclopentene from cyclopentadiene by hydrogenating cyclopentene with hydrogen gas at a ratio of 1 to 1.5 moles of hydrogen per mole of cyclopentadiene in the presence of a palladium catalyst on a carrier.

US patent no. 4108911, issued on August 22, 1978, relates to a process for preparation of cyclopentene that comprises selectively hydrogenating cyclopentadiene in the liquid phase by contacting cyclopentadiene with hydrogen in the presence of a hydrogenation catalyst comprising a highly dispersed form of nickel selected from the group consisting of Raney nickel or a modified Raney nickel in which a polyol selected from the group consisting of 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2,3-propanetriol, 1,2-butanediol, 1,4-butanediol, 1,3-butanediol, 1,2,4-butanetriol and 1,2,3-propanetriol is employed in the reaction mixture in the volume ratio of the polyol to cyclopentadiene of from 1/1 to 4/1.

US patent no. 4131629, issued on December 26, 1978, discloses preparation of cyclopentene which comprises of selective hydrogenation of cyclopentadiene using Raney nickel or T1-

modified Raney-nickel in water medium. The volume ratio of cyclopentadiene and water ranges from 1:1 to 1:4. The hydrogenation took place at temperature ranges from 20 °C to 30 °C and the hydrogen pressure at 150 psig to 1035.5 psig. In this prior art, the maximum conversion of cyclopentadiene was 93.6% where 88.4% of cyclopentene and 11.5% of cyclopentane was obtained. The hydrogenation took place at 25 °C, hydrogen pressure 250-300 psig and time 45 mins. However, this requires a huge amount of Raney nickel to be present as catalysts for the reaction to take place, which is disadvantageous.

US patent no. 4167529, issued on September 11, 1979, further discloses selective hydrogenation of cyclopentadiene to cyclopentene using Raney Nickel catalyst and ammonium hydroxide in the reaction mixture.

Further, US patent no. 4155943, issued on May 22, 1979 relates to a process for selective hydrogenation of cyclopentadiene to cyclopentene using Raney Nickel catalyst and surfactants. US patent no. 4162271, issued on July 24, 1979, discloses selective hydrogenation of cyclopentadiene to cyclopentene using Raney Nickel catalyst and alcohol (boiling above 99°C) in the reaction mixture.

Furthermore, there are some prior arts that report hydrogenation of cyclooctadiene and other cyclic polyolefins. For example, US patent No. 3316319, issued on April 25, 1967 discloses a process for selective hydrogenation of non-conjugated cyclic polyolefins like by reaction with molecular hydrogen in the presence of a catalyst, the improvement which comprises carrying out said reaction at a temperature of 25 to 150°C and a pressure up to 100 atmospheres in contact with a divalent palladium catalyst and water.

US patent No. 3418386, issued on December 24, 1968 discloses a process for a selectively hydrogenating one of the double bonds of a cyclooctadienyl nucleus, wherein hydrogen is reacted with the unsaturated hydrocarbons in the presence of palladium catalyst under pressure and temperature.

5

However, all the above reported hydrogenation processes suffer from the drawbacks of obtaining unsatisfactory conversion rates of cyclic di-olefins to cyclic mono-olefins and also being highly expensive or environmentally unfriendly methods, so much so that their industrial scale-up becomes unrealistic.

10

It has further been noted that the most common catalysts used in the above reported hydrogenation processes are either conventional pyrophoric nickel metal catalyst i.e. Raney nickel (Ni) or palladium or rhodium and ruthenium. As known in the art, conventional Raney Ni is prepared by dissolving nickel in molten aluminium followed by quenching. Further, such
15 process requires repeated washing with solvents and alkali solutions to obtain the final porous Raney nickel particles. This renders the Raney Ni catalysts obtained to be of serious environmental hazard when used in larger amounts, along with a lower catalytic efficiency. On the other hand, palladium or rhodium or ruthenium catalysts are too expensive to be used in an industrial scale. Some other catalysts known in the relevant art are compound catalysts
20 comprising two or more metals in a mixture or alloyed as for example, silver-copper, copper-chromium, copper-zinc, nickel-zinc etc. Such catalysts are complex to prepare and thus are not easily scalable to an industrial level. Hence, it is desirable to utilize low cost, lesser amounts, easily scalable, yet efficient and environmentally friendly catalytic materials in order to achieve green chemistry in cyclic mono-olefin production by hydrogenation reaction.

25

Although, CN103480394A discloses a novel modified Raney nickel catalyst, prepared by dipping Raney nickel in a modifying agent, followed by ultrasonic treatment; however, such a catalyst has been specifically adaptedfor glucose hydrogenation reaction of sorbitol and not for any selective hydrogenation process in cyclic di-olefins. Moreover, in this prior reported method, sonication was used for leaching and not necessarily for getting finer particles.

Further, Meng, Qi et. al.: Cuihua Xuebao, volume 25, issue 7, pages 529-532 discloses that ultrasonic wave when applied during the alkaline leaching process of Ni - Al mother alloy, results into formation of a novel Raney Ni catalyst. With the increase in sonication time, the catalyst activity first increased and then decreased gradually. However, the said catalyst was specifically adapted for saturated hydrogenation of benzene to cyclohexane and not for any selective hydrogenation process in cyclic di-olefins.

Therefore, there still exists a need in the art to develop a simple, environment friendly and cost-effective process for producing cyclic mono-olefins from their corresponding cyclic di-olefins with better conversion rates. Accordingly, the present inventors have developed a green, practical, easily scalable and economical method for selective hydrogenation of one of the two double bonds of any cyclic di-olefin, essentially in presence of a sonicated S1-modified Raney-Nickel, for producing its corresponding cyclic mono-olefin with higher conversion rate and selectivity.

OBJECTS OF THE INVENTION

It is an object of the present invention to provide a simple, economical and industrially scalable catalytic hydrogenation process for preparing cyclic mono-olefins from their corresponding

cyclic di-olefins, wherein the catalysts involved is essentially a leached and sonicated S1-modified Raney-Nickel in a small amount of 1-2 wt%.

It is another object of the present invention to provide a catalytic hydrogenation process for selective hydrogenation of one of the two conjugated double bonds of the treated cyclic di-olefin to produce its corresponding cyclic mono-olefin in a liquid phase, essentially in presence of an active hydrogenation catalyst S1-modified Raney-Nickel under pressure and temperature which are substantially less than the stoichiometrical amount of hydrogen theoretically required to completely reduce the cyclic diene to the corresponding cyclic mono-olefin.

It is yet another object of the present invention to provide a catalytic hydrogenation process of cyclic di-olefins at a lower temperature and pressure range of 50-100^{o}C and 400-500psig respectively, for preparing their corresponding cyclic mono-olefins.

It is yet another object of the present invention to provide a simple, economical and industrially scalable catalytic hydrogenation process for preparing cyclopentene from cyclopentadiene with a conversion rate of about 99-100% and selectivity of around 88%; and other cyclic mono-olefins like cyclooctene and cyclohexene formation with around 95-100% conversion rate and around 88-98% selectivity.

It is yet another object of the present invention to provide a green catalytic hydrogenation process for preparing cyclic mono-olefins.

SUMMARY OF INVENTION

One aspect of the present invention provides a process for selective catalytic hydrogenation of a cyclic di-olefin to its corresponding cyclic mono-olefin comprising subjecting the cyclic di-olefin to hydrogenation in presence of sonicated S1-modified Raney Nickel (Ni) catalyst.

Another aspect of the present invention provides a process for selective catalytic hydrogenation of a cyclic di-olefin to its corresponding cyclic mono-olefin comprising steps of:

i) adding a cyclic di-olefin and a solvent into a reaction vessel; and

ii) conducting the selective hydrogenation reaction by chargingsonicated S1-modified Raney Nickel (Ni) catalyst into the vessel.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

The above and other aspects, features, and advantages of certain exemplary embodiments of the present invention will be more apparent from the following description taken in conjunction with the accompanying drawings in which:

Figure 1 illustrates comparative particle size data between sonicated Raney-Ni used in the present invention and normal Raney-Ni (unsonicated);

Figure 2 illustrates 1H NMR data of Cyclopentene prepared by the hydrogenation process of the present invention involving S1-modified Raney-Nickel catalyst;

Figure 3 illustrates 1H NMR data of Cyclohexene prepared by the hydrogenation process of the present invention involving S1-modified Raney-Nickel catalyst;

Figure 4 illustrates the comparative 1H NMR data between a) Cyclopentene prepared by the hydrogenation process of present invention essentially involving S1-modified Raney-Nickel catalysts and b) that produced by conventional process involving normal Raney-Nickel catalyst;

Figure 5 illustrates the comparative 1H NMR data between a) Cyclohexene prepared by the hydrogenation process of present invention essentially involving S1-modified Raney-Nickel catalysts and b) that produced by conventional process involving normal Raney-Nickel catalyst;

Persons skilled in the art will appreciate that elements in the figures are illustrated for simplicity and clarity and may have not been drawn to scale. For example, the dimensions of some of the elements in the figure may be exaggerated relative to other elements to help to improve understanding of various exemplary embodiments of the present disclosure. Throughout the drawings, it should be noted that like reference numbers are used to depict the same or similar elements, features, and structures.

DETAILED DESCRIPTION OF THE INVENTION

The following description with reference to the accompanying drawings is provided to assist in a comprehensive understanding of exemplary embodiments of the invention. It includes various specific details to assist in that understanding but these are to be regarded as merely exemplary.

Accordingly, those of ordinary skill in the art will recognize that various changes and modifications of the embodiments described herein can be made without departing from the scope of the invention. In addition, descriptions of well-known functions and constructions are omitted for clarity and conciseness.

The terms and words used in the following description and claims are not limited to the bibliographical meanings, but, are merely used by the inventor to enable a clear and consistent understanding of the invention. Accordingly, it should be apparent to those skilled in the art that the following description of exemplary embodiments of the present invention are provided for illustration purpose only and not for the purpose of limiting the invention as defined by the appended claims and their equivalents.

It is to be understood that the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise.

Features that are described and/or illustrated with respect to one embodiment may be used in the same way or in a similar way in one or more other embodiments and/or in combination with or instead of the features of the other embodiments.

It should be emphasized that the term "comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

The term 'S1-modified Raney-Nickel' as used herein refers to normal Raney-Nickel that was leached and sonicated by a process as described in the present invention;

The term 'economical' as used herein refers to the catalytic hydrogenation process of the present invention that essentially requires a very less amount of Raney-Ni for effective hydrogenation reaction to take place and whereby, the said catalyst can be recovered and reused, rendering it be a cost-effective process;

The term 'green chemistry' as used herein refers to a hydrogenation process of the present invention that essentially uses water as a solvent and does not involve any other hazardous solvents, thus making it environment-friendly;

The term 'higher conversion rate' as used herein refers to 99-100% conversion rate of a cyclic di-olefin to its corresponding cyclic mono-olefin;

The term 'PA reactor' as used herein refers to 'stirred stainless steel chemical reactor' obtained from Parr Instrument Company;

The term 'psig' as used herein is an abbreviated form of pressure measuring unit 'pounds per square inch gauge';

The term 'NMR' as used herein refers to 'Nuclear Magnetic Resonance';

The term 'GCMS' as used herein refers to 'Gas Chromatography-Mass Spectroscopy'.

The present invention provides a green, simple, easily scalable and economical process for selective hydrogenation of any cyclic di-olefin to its corresponding cyclic mono-olefin with higher conversion rate and selectivity.

An embodiment of the present invention relates to a process for selective catalytic hydrogenation of a cyclic di-olefin to its corresponding cyclic mono-olefin comprising subjecting the cyclic di-olefin to hydrogenationin presence of sonicated S1-modified Raney Nickel (Ni) catalyst.

The present process advantageously utilizes a very small amount of said catalyst which is around 1-2 wt%, thus making the current process economical, greener and industrially scalable.

Another embodiment of the present invention provides a process for selective catalytic hydrogenation of a cyclic di-olefin to its corresponding cyclic mono-olefin comprising steps of:

i) adding a cyclic di-olefin and a solvent into a reaction vessel;

ii) conducting the selective hydrogenation reaction by charging sonicated S1-modified Raney Nickel (Ni) catalyst into the vessel.

The hydrogenation process of the present invention as mentioned above is conducted for a time period of 1- 1.5 hours in a liquid phase, wherein the solvent used is water and the ratio between the cyclic di-olefin and the solvent is in the range of 1:4 to 1:2. Use of water as a solvent renders the current process economical, simple and easily scalable. Advantageously, the present process is devoid of using any additional environment polluting solvents, hence supports green chemistry. The reaction vessel used is preferably a stirred stainless steel chemical reactor.

Further, in accordance with the present invention, the sonicated S1-modified Raney Nickel (Ni) catalyst is in the range of 1-2wt%.

Typically, the conducting of the selective hydrogenation reaction is carried out at a temperature range of 50-100°C under hydrogen pressure in the range of 400-500 psig.

Further, in accordance with the present invention, the catalyst used for the hydrogenation reaction of cyclic di-olefins is essentially a sonicated S1-modified Raney Nickel (Ni). It is prepared by alkaline leaching of conventional Raney Ni, preferably with 3-20% aqueous sodium hydroxide solution; followed by sonication for 15-30 mins. The sonicated S1-modified Raney Ni catalyst thus obtained has a finer particle size and greater active specific surface area compared to the conventional Raney nickel that does not undergo ultrasonic treatment. As a result, it has been found that the sonicated S1-modified Raney Ni catalyst as used in the present process provides better conversion rate of a cyclic di-olefin to cyclic mono-olefin with higher selectivity, in comparison to the results obtained by using a normal unsonicated Raney Ni as catalyst in a similar hydrogenation reaction. The same has been discussed in details later under example section.

Furthermore, in the present invention, the pressure ranges from 400psig -500psig and the temperature ranges from 50 °C-100 °C. Such pressure and temperature as used in the currently developed process are substantially less than the stoichiometrical amount of hydrogen

theoretically required to completely reduce the cyclic diene to the corresponding cyclic mono-olefin. Moreover, lower operating temperatures are preferable, since higher temperatures frequently result in a decreased yield for the desired mono-olefin due to polymerization and other undesirable side reactions.

The class of cyclic di-olefins that can undergo selective catalytic hydrogenation reaction of the present invention having all of its carbon atoms in the salicylic ring is selected from cyclopentadiene, 1,5-cyclooctadiene, 1,3-cyclohexadiene, 1,4-cyclohexadiene etc. The corresponding cyclic mono-olefins formed as a result of the currently developed hydrogenation process are cyclopentene, cyclooctene, cyclohexene etc.

The present invention thus advantageously provides a practical, economical and green process for selective hydrogenation of one of the two double bonds of a cyclic di-olefin to produce its corresponding cyclic mono-olefin. The currently developed process is applicable to the conversion of any cyclic di-olefins containing two double bonds in conjugated as well as non-conjugated relationship in the alicyclic ring to the corresponding cyclic mono-olefins containing the same number of carbon atoms. In this invention, the cyclic olefin containing at least two double bonds is converted to cyclic mono-olefin with around 95-100% conversion rate and 88-98% selectivity, which is of considerable importance since this can afford molecules having a single point of attack at which certain reactions can be applied to form compounds useful in industry.

The invention is now illustrated by way of non-limiting examples. The examples are intended to be purely exemplary of the invention, should therefore not be considered to limit the invention in any way.

EXAMPLES

EXAMPLE 1: Process for preparing sonicated S1-modified Raney Ni catalysts for the present invention

Example 1 illustrates the process for preparing sonicated S1-modified Raney Ni which is utilized as an active catalyst in the hydrogenation reaction of the present invention.

Procedure: The S1-modified Raney Nickel (Ni) catalyst is prepared by a process comprising steps of: a) adding conventional Raney-Ni portion wise to 20% aq. NaOH solution; b) heating at 90 °C for 2hrs; c) washing with 3% aq. NaOH solution; d) boiling at 90 °C with 20% aq. NaOH solution; further e) washing with water; followed by f) ultrasonic treatment for 30 mins.

Result: As illustrated by the comparative images of accompanying figure 1, the sonicated S1-modified Raney Ni prepared by the above process obtained finer particle size and higher active surface area in comparison to larger particle size of normal Raney-Nickel (unsonicated). This indicates that the S1-modified Raney Ni prepared by the above process is more catalytically active than normal Raney Ni. The following examples confirm the same.

EXAMPLE 2: Preparation of Cyclopentene from Cyclopentadiene

Example 2 illustrates the process for preparation of cyclopentene from cyclopentadiene by the selective catalytic hydrogenation reaction of the present invention involving the S1-modified Raney Ni catalysts of example 1.

Procedure: A 600ml stirred stainless steel chemical reactor is charged with 200ml water containing 500mg of S1-modified Raney-nickel (30 min sonicated) of example 1, followed by addition of 50g of freshly distilled cyclopentadiene. The sealed reactor is then charged with hydrogen gas at 500psig while stirring. The reactor is set at 50 °C and after 15 mins the internal

temperature of the reaction mixture was raised to 82 °C. The reaction is stopped after 1h and 15 mins.

Results: The 1H NMR analysis data as illustrated in accompanying figure 2 shows that that ~99% conversion of cyclopentadiene has occurred, of which ~88% selectively is cyclopentene, ~10% is cyclopentane, and ~2% is dicyclopentadiene.

EXAMPLE 3: Preparation of Cyclohexene from Cyclohexadiene

Example 3 illustrates the process for preparation of cyclohexene from cyclohexadiene by the selective catalytic hydrogenation reaction of the present invention involving the S1-modified Raney Ni catalyst of example 1.

Procedure: A 100 ml stainless steel chemical reactor is charged with 40ml water containing 200mg of S1-modified Raney-nickel (30 min sonicated) of example 1 and 10g of 1,3-cyclohexadiene. The sealed reactor is then charged with 500 psig of hydrogen with stirring. The reactor is held at 100 °C. The reaction is stopped after 1 hr 30 min.

Result: The 1H NMR analysis as illustrated in accompanying figure 3 shows that 100% conversion of 1, 3-cyclohexadiene has occurred of which 95% is selectively cyclohexene with trace amounts of cyclohexane.

Accordingly, the results obtained by the hydrogenation reactions of the present invention as conducted in examples 2, 3 above is depicted in table 1 below:

Table 1

Name of the	Reactant	Reacti	Temperatur	Products	Selectivit	Conversion

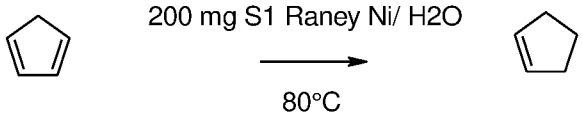
Reactant (cyclic diene)	Amount	on Time	e	(cyclic mono olefin)	y (%)	rate (%)
Cyclopentadiene	50 gm	1hr 30 min	50 °C-80 °C	Cyclopentene	88	99
1,3-cyclohexadiene	10 gm	1hr 30 min	100 °C	Cyclohexene	95	100

EXAMPLE 4: A comparative study between products / results obtained by using sonicated Raney-Ni over normal unsonicated Raney-Ni in selective hydrogenation of cyclopentadiene

Example 4 illustrates comparative 1H NMR study between the cyclic mono-olefinic products obtained by the hydrogenation reaction of the present invention essentially involving S1-modified Raney-Nickel catalyst of example 1 and that obtained when normal unsonicated Raney-Nickel is used as catalyst.

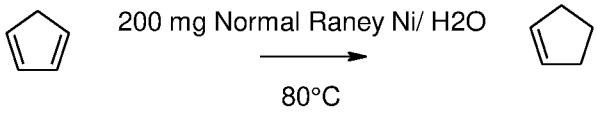
Procedure:

a) With 200 mg S1-modified Raney-Ni catalyst:



In a 100 ml stirred chemical reactor (PA-1), 10 gm cyclopentadiene is charged with 200 mg S1-modified Raney-Ni catalyst of example 1, in 20ml water. The said reactor is then charged with 500psig H2 pressure. Reaction mixture is next stirred at 80 °C for 1 hr 30 mins. Then reaction is stopped and cool down to room temperature. The reaction mixture is next separated by means of a separating funnel and dried over sodium sulphate (Na_2SO_4).

b) With 200 mg Normal Unsonicated Raney-Ni as catalyst:



In a 100 ml PA reactor (PA-1), 10 gm cyclopentadiene is charged with 200 mg normal unsonicated Raney-Ni in 20ml water. The said reactor is then charged with 500psig H2 pressure. The reaction mixture is stirred at 80 °C for 1 hr 30 mins. Then the reaction is stopped and cool down to room temperature. The reaction mixture is next separated by means of a separating funnel and dried over Na_2SO_4.

Results:

Figure 4 represents comparative 1H NMR data that shows below:

a) ~100% conversion of 1,5 cyclopentadiene occurs with 97% selectivity towards cyclopentene production (along with 3% cyclopentane and very trace amounts of starting material) by the hydrogenation reaction of the present invention essentially involving sonicated S1-modified Raney-Ni catalyst of example 1; whereas,

b) only ~60% conversion of 1,5 cyclopentadiene occurs with 80% selectivity towards cyclopentene formation (along with 10% cyclopentane,10% DCPD and 40% starting material), in case of the hydrogenation reaction conducted using unsonicated normal Raney Ni catalyst.

Such comparative data confirms the better working of the currently developed hydrogenation process over the conventional ones in view of the higher conversion rate of cyclic di-olefin e.g. 1,5 cyclopentadiene achieved that produces corresponding cyclic mono-olefins e.g. cyclopentene with superior selectivity.

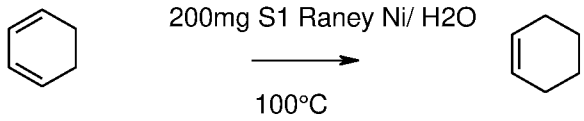
EXAMPLE 5: A comparative study between products / results obtained by using sonicated Raney-Ni over normal unsonicated Raney-Ni in selective hydrogenation of cyclohexadiene

Example 5 illustrates comparative 1H NMR study between the cyclic mono-olefinic products obtained by the hydrogenation reaction of the present invention essentially involving S1-

modified Raney-Nickel catalyst of example 1 and that obtained when normal unsonicated Raney-Nickel is used as catalyst.

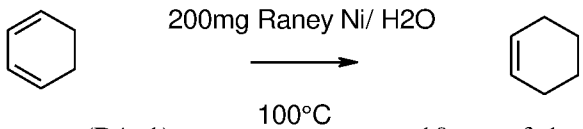
Procedure:

a) With 200mg S1-modified Raney-Ni catalyst:



In a 100 ml stirred chemical reactor (PA-1), 10gm of 1, 3-cyclohexadiene is charged with 200 mg S1-modifed Raney-Ni catalyst of example 1, in 20ml water. Then 500 psig H2 pressure is charged on the reaction mixture. The said reaction mixture is stirred for 2 hr at 100 °C. Then the reaction is stopped and cool down to room temperature. The reaction mixture is next separated by means of a separating funnel and dried over Na_2SO_4.

b) With 200 mg Unsonicated Normal Raney-Ni:



In a 100 ml PA reactor (PA-1), 10gm of 1, 3-cyclohexadiene is charged with 200mg unsonicated normal Raney Ni in 40ml water. Then 500psig H2 pressure is charged on the reaction mixture. The said reaction mixture is stirred for 2 hr at 100 °C. Then the reaction is stopped and cool down to room temperature. The reaction mixture is separated by means of a separating funnel and dried over Na_2SO_4.

Results:

Figure 5 represents comparative 1H NMR data that shows below:

a) ~95% conversion of 1,3- cyclohexadiene occurs with 98% selectivity towards cyclohexene production (along with 2% cyclohexane and 5% starting material) by the hydrogenation reaction

of the present invention essentially involving sonicated S1-modified Raney-Ni catalyst of example 1; whereas,

b) only 60% conversion of 1,3- cyclohexadiene occurs with 80% selectivity towards cyclohexene production (along with 20% cyclohexane and 40 % starting material), in case of the hydrogenation reaction conducted using unsonicated normal Raney Ni catalyst.

Such comparative data confirms the better working of the currently developed hydrogenation process over the conventional ones in view of the higher conversion rate of cyclic di-olefin e.g. 1,3- cyclohexadiene achieved that produces corresponding cyclic mono-olefins e.g. cyclohexene with superior selectivity.

CLAIMS:

1. A process for selective catalytic hydrogenation of a cyclic di-olefin to its corresponding cyclic mono-olefin comprising subjecting said cyclic di-olefin to hydrogenation in presence of sonicated S1-modified Raney Nickel (Ni) catalyst.

2. The process as claimed in claim 1, wherein the sonicated S1-modified Raney Nickel (Ni) catalyst is in the range of 1-2wt%.

3. A process for selective catalytic hydrogenation of a cyclic di-olefin to its corresponding cyclic mono-olefin comprising steps of:
    a. adding a cyclic di-olefin and a solvent into a reaction vessel; and
    b. conducting the selective hydrogenation reaction by charging sonicated S1-modified Raney Nickel (Ni) catalyst into said vessel.

4. The process as claimed in claim 3, wherein the cyclic di-olefin and the solvent is in a volume ratio of 1:4 to 1:2.

5. The process as claimed in claim 3, wherein the sonicated S1-modified Raney Nickel (Ni) catalyst is in the range of 1-2wt%.

6. The process as claimed in claim 1 or claim 3, wherein the selective hydrogenation reaction is conducted at a temperature range of 50-100°C under hydrogen pressure range of 400-500 psig.

7. The process as claimed in claim 1 or claim 3, wherein the S1-modified Raney Nickel (Ni) catalyst has undergone sonication for 15-30 mins.

8. The process as claimed in claim 7, wherein Raney Nickel (Ni) has undergone alkaline leaching before sonication, preferably by 3-20% aqueous sodium hydroxide (NaOH).

9. The process as claimed in claim 1 or claim 3, wherein the hydrogenation reaction is conducted for a time period of 1-1.5 hours.

10. The process as claimed in claim 1 or claim 3, wherein the hydrogenation reaction is conducted in a liquid phase.

11. The process as claimed in claim 3, wherein the solvent is water.

12. The process as claimed in claim 3, wherein the reaction vessel is a stirred stainless steel chemical reactor.

13. The process as claimed in claim 1 or claim 3, wherein the cyclic di-olefin is selected from cyclopentadiene, 1,5-cyclooctadiene, 1,3-cyclohexadiene or 1,4 cyclohexadiene.

14. The process as claimed in claim 1 or claim 3, wherein the cyclic mono-olefin is selected from cyclopentene, cyclooctene or cyclohexene.

15. The process as claimed in any of the preceding claims provides 95-100% conversion rate of a cyclic di-olefin to its corresponding cyclic mono-olefin.

16. The process as claimed in claim 15 provides 99-100% conversion rate of cyclopentadiene to cyclopentene.

17. The process as claimed in claims 1-14 provides 88-98% selectivity towards cyclic mono-olefin production.

5

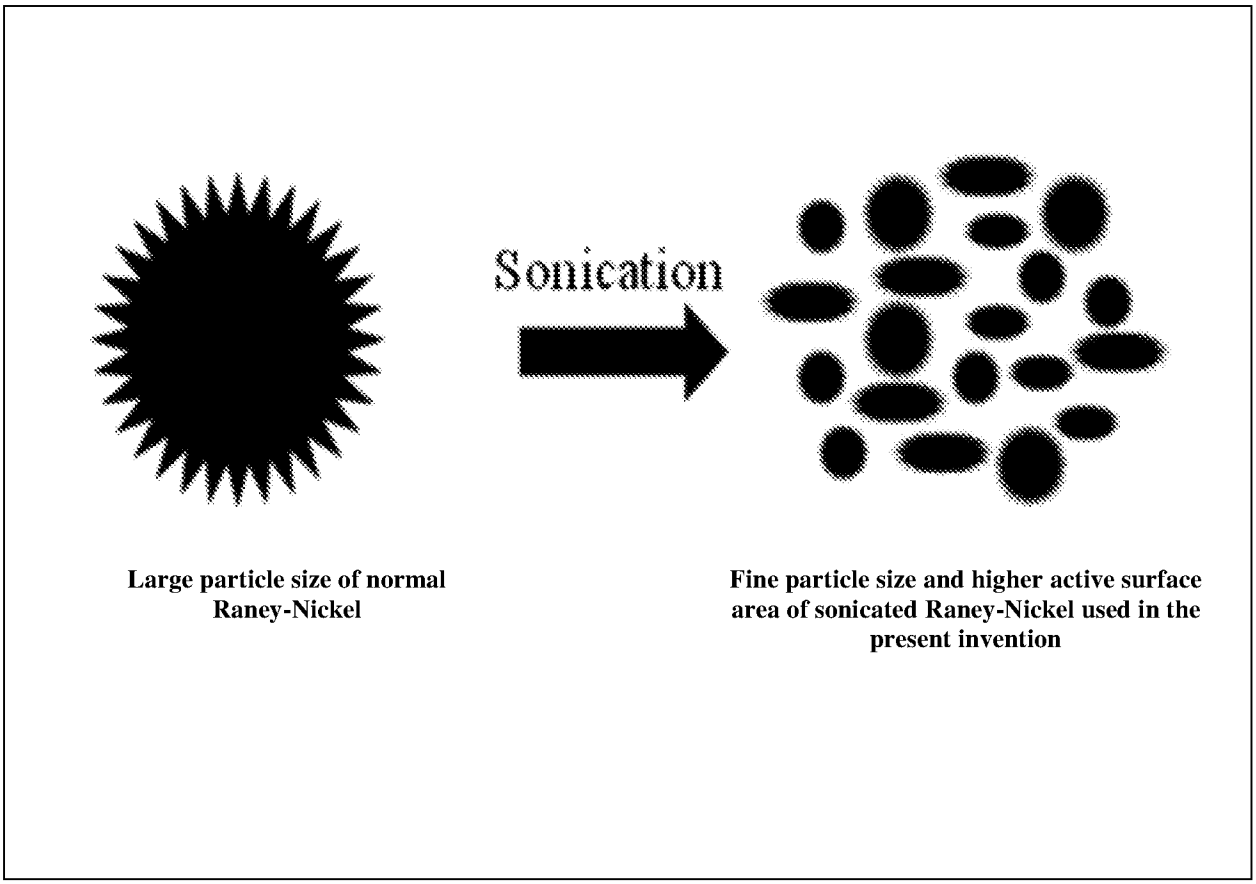

Sonication
Large particle size of normal Raney-Nickel
Fine particle size and higher active surface area of sonicated Raney-Nickel used in the present invention

Figure 1

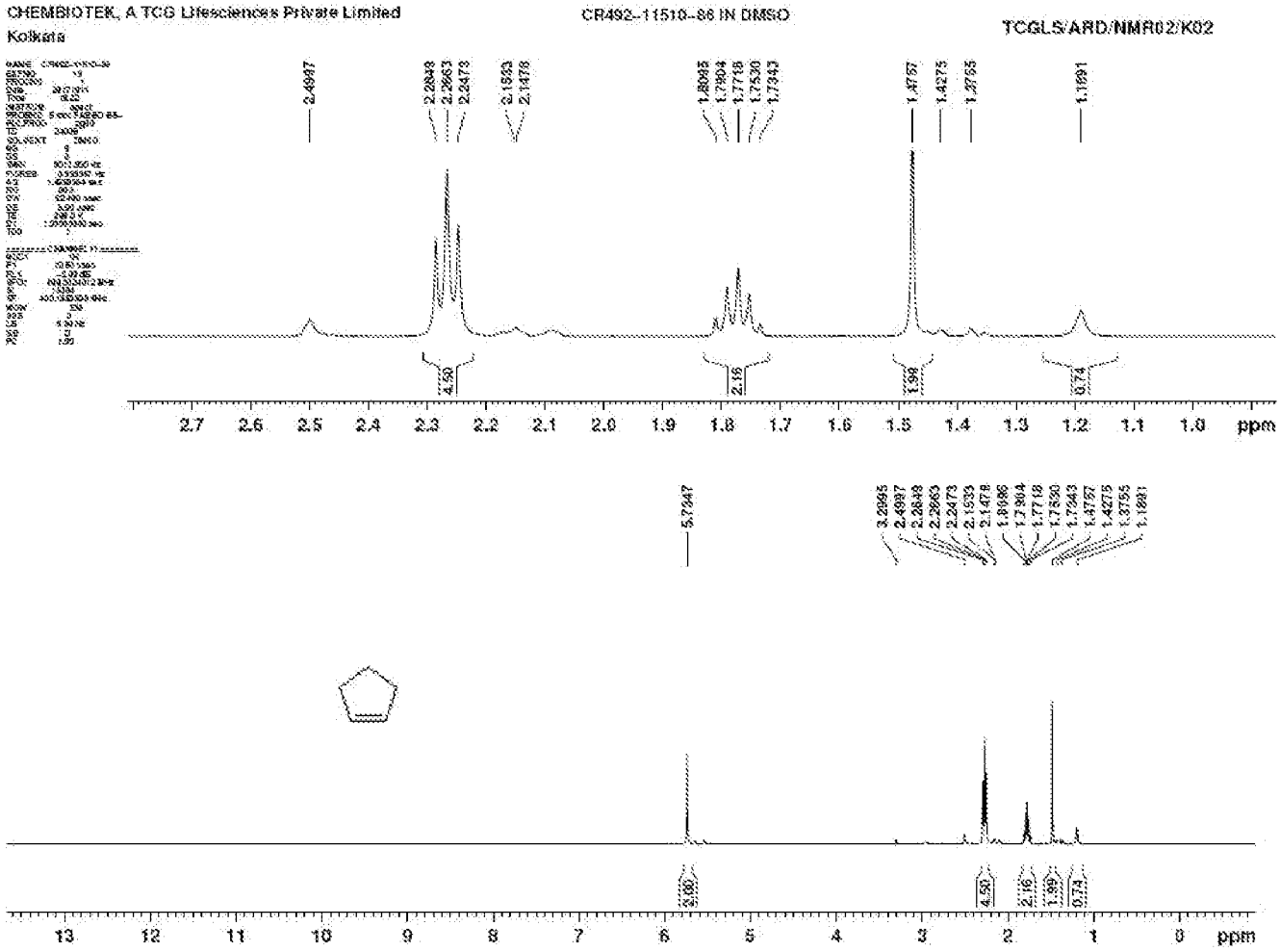

CHEMBIOTEK, A TCG Lifesciences Private Limited
Kolkata
CR492-11510-86 IN DMSO
TCGLS/ARD/NMR02/K02
2.4997
2.2848
2.2663
2.2473
2.1533
2.1478
1.8095
1.7904
1.7718
1.7530
1.7343
1.4757
1.4275
1.3765
1.1691
4.50
2.16
1.99
0.74
ppm
5.7347
3.2995
2.4997
2.2848
2.2663
2.2473
2.1533
2.1478
1.8095
1.7904
1.7718
1.7530
1.7343
1.4757
1.4275
1.3755
1.1691
2.00
4.50
2.16
1.99
0.74
ppm

Figure 2

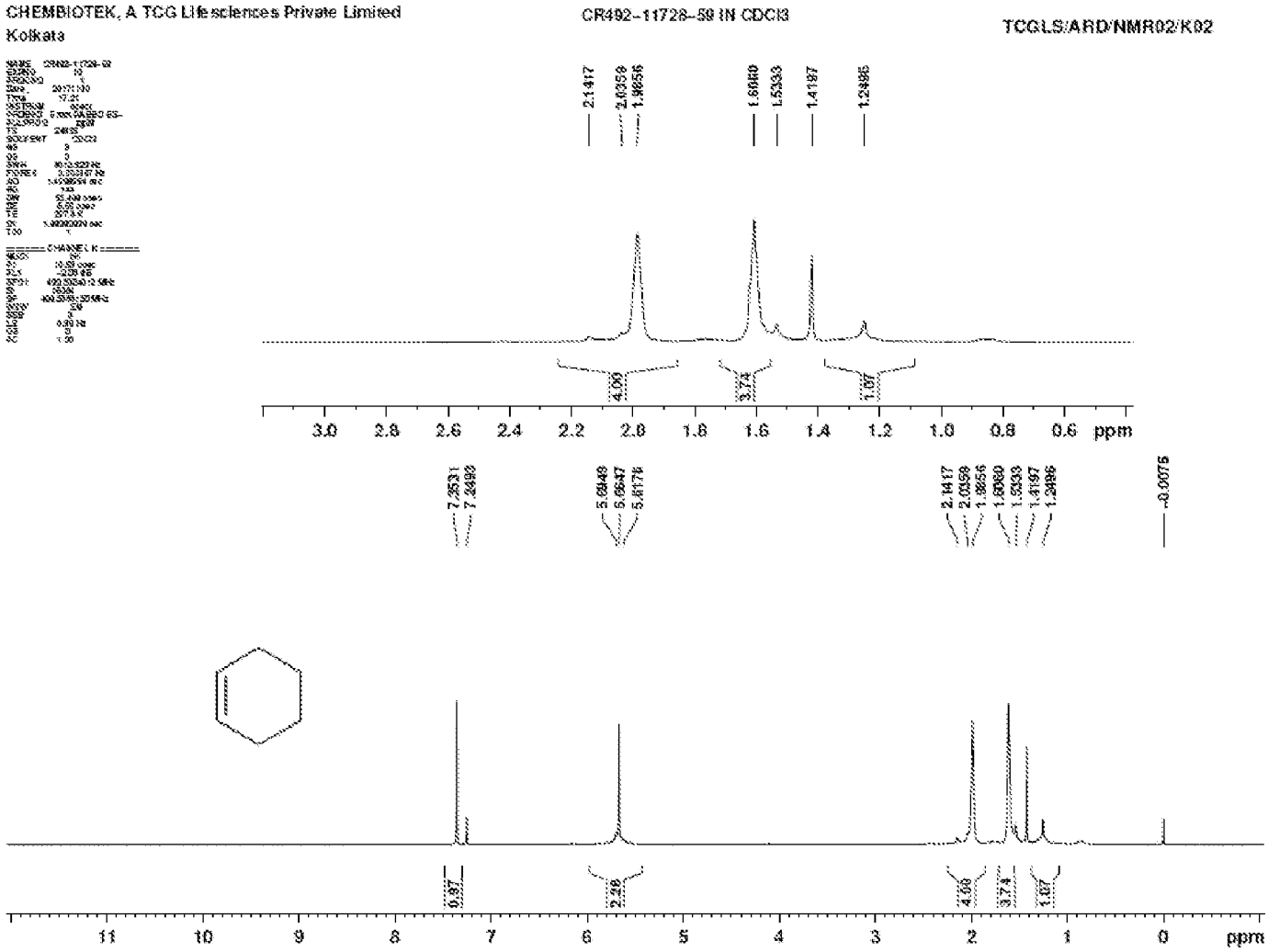

CHEMBIOTEK, A TCG Lifesciences Private Limited
Kolkata
CR492-11728-58 IN CDCl3
TCGLS/ARD/NMR02/K02
2.1417
2.0359
1.9656
1.6040
1.5333
1.4197
1.2486
4.00
3.74
1.07
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 ppm
7.2531
7.2498
5.6948
5.6647
5.6176
2.1417
2.0359
1.9656
1.6040
1.5333
1.4197
1.2486
-0.0076
0.97
2.26
4.00
3.74
1.07
11 10 9 8 7 6 5 4 3 2 1 0 ppm

Figure 3

a)

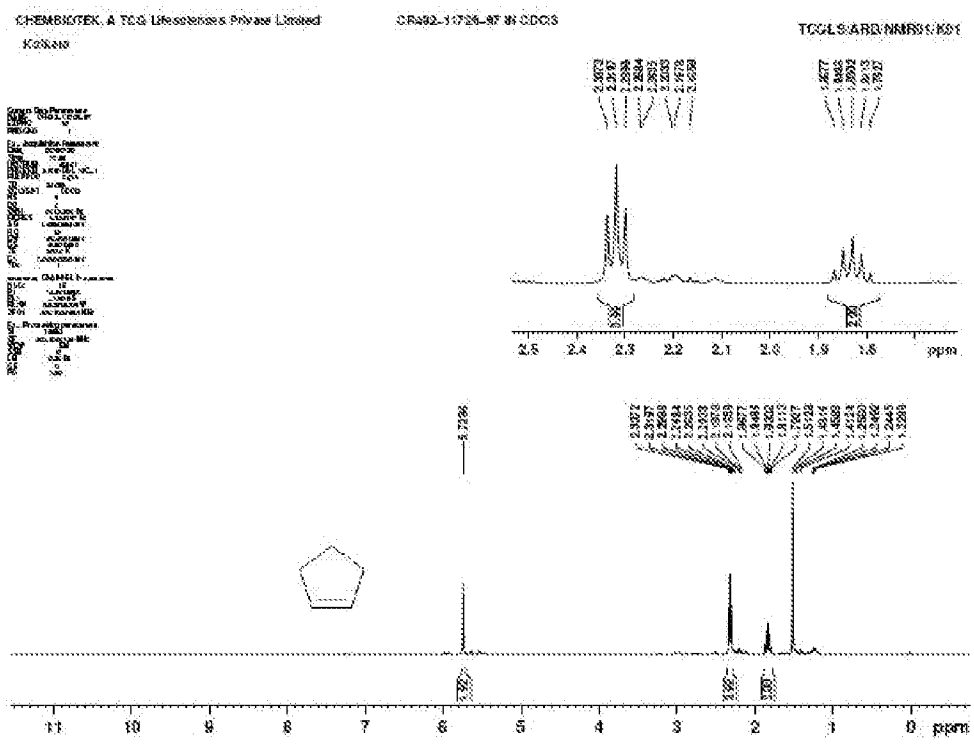

CHEMBIOTEK, A TCG Lifesciences Private Limited
Kolkata
TCGLS/ARD/NMR/1/601
2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm

Figure 4a

b)

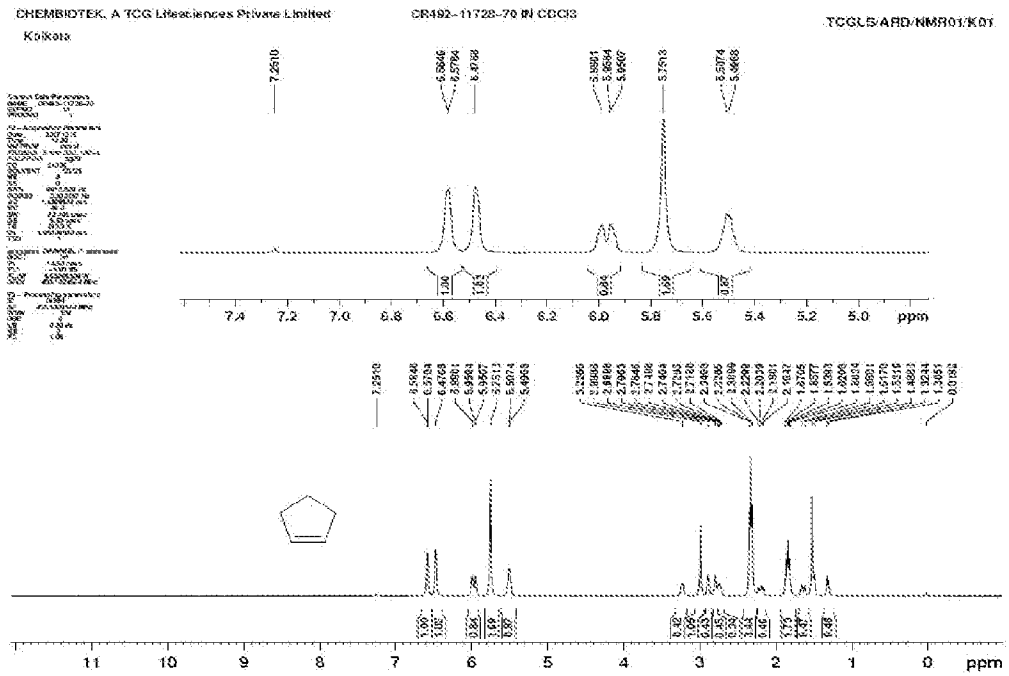

CHEMBIOTEK, A TCG Lifesciences Private Limited
Kolkata
CR492-11728-70 IN CDCl3
TCGLS/ARD/NMR01/K01
ppm

Figure 4b

a)

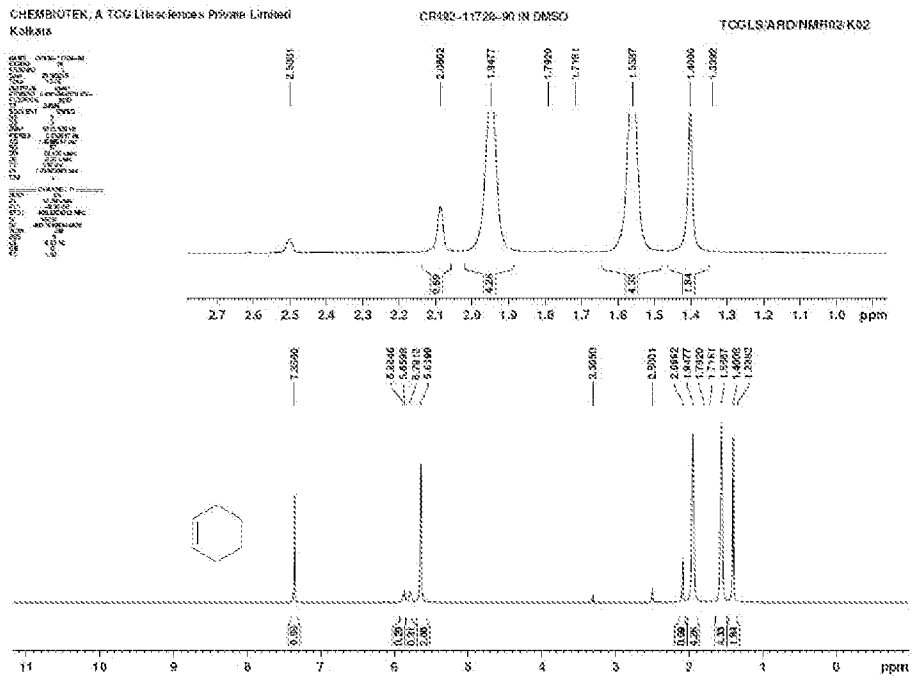

CHEMBIOTEK, A TCG Lifesciences Private Limited
Kolkata
CR482-11726-90 IN DMSO
TCGLS\ARD\NMR\02\K02
2.5051
2.0962
1.9477
1.7909
1.7161
1.5587
1.4066
1.3362
ppm
7.3596
5.8246
5.6598
5.6190
3.3650
2.5051
2.0962
1.9477
1.7909
1.7161
1.5587
1.4066
1.3362
ppm

Figure 5a

b)

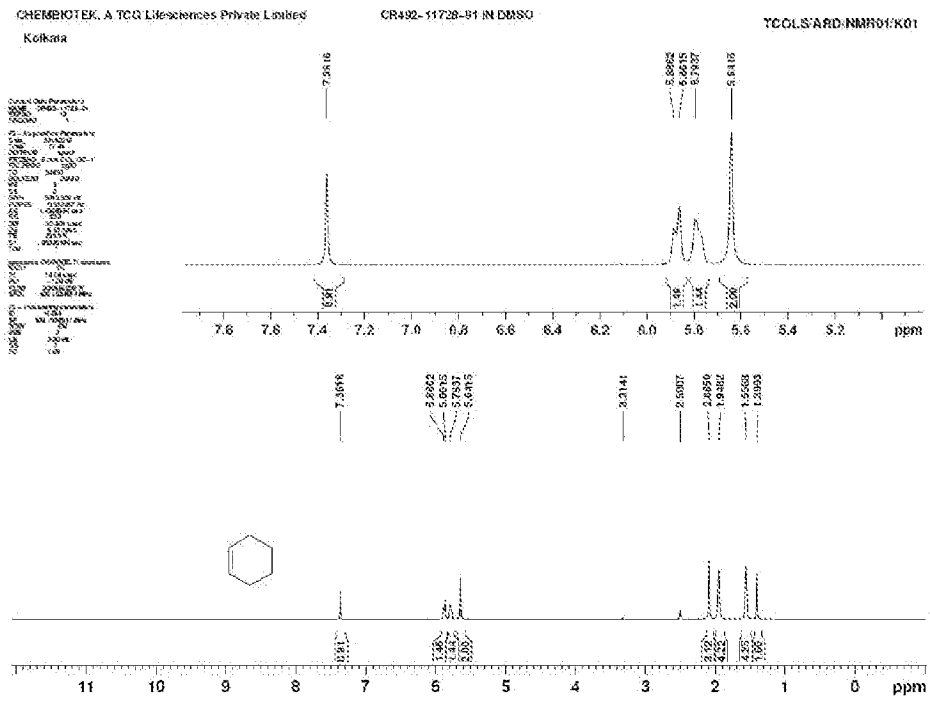

CHEMBIOTEK, A TCG Lifesciences Private Limited
Kolkata
CR492-11728-81 IN DMSO
TCGLS/ARD/NMR01/K01
7.5516
5.8862
5.6615
5.7937
5.6415
7.5516
5.8862
5.6615
5.7937
5.6415
3.3141
2.5057
2.4650
1.9482
1.5583
1.2393
ppm
ppm

Figure 5b

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2018/050597

A. CLASSIFICATION OF SUBJECT MATTER
C07C13/15,C07C13/23,C07C23/263,C07C5/05,B01J25/02 Version=2019.01

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)

C07C, 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)

TotalPatent One, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4131629 A (THE GOODYEAR TIRE AND RUBBER CO[US]), 26 December 1978 (26-12-1978) Abstract, Claims, Description	1-17
Y	US 4162271 A (THE GOODYEAR TIRE AND RUBBER CO[US]), 24 July 1979 (24-07-1979) Abstract, Claims, Description	1-17
Y	US 4167529 A (THE GOODYEAR TIRE AND RUBBER CO[US]), 11 September 1979 (11-09-1979) Abstract, Claims, Description	1-17
Y	CN 103480394 A (UNIV SHANGHAI[CN]), 1 January 2014 (01-01-2014) Abstract, Claims, Description	1-17
Y	"Preparation of Raney Ni by Ultrasonic Wave and Its Catalytic Activity in Benzene Hydrogenation", Meng, Qi et. al.; Cuihua Xuebao, volume 25, issue 7, pages 529-532, 2004 Abstract	1-17
Y	"Ultrasonically Induced Enhancement of Isotope-Exchange Catalysts: Surface Analysis of	

☒ 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	Date of mailing of the international search report
18-02-2019	18-02-2019
Name and mailing address of the ISA/ Indian Patent Office Plot No.32, Sector 14,Dwarka,New Delhi-110075 Facsimile No.	Authorized officer Subhankar Panda Telephone No. +91-1125300200

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2018/050597

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Raney Nickel Alloys", Eugene A. Cioffi et. al.; Langmuir, 1988, 4, 697-702 Abstract, page 699	1-17

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IN2018/050597

Citation	Pub.Date	Family	Pub.Date
US 4131629 A	26-12-1978	CA 1092614 A	30-12-1980
US 4162271 A	24-07-1979	DE 2848698 A1	17-05-1979
		GB 2007707 A	23-05-1979
		FR 2408563 A1	08-06-1979
		CA 1099298 A	14-04-1981
US 4167529 A	11-09-1979	BE 871810 A	01-03-1979
		CA 1099299 A	14-04-1981