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(54) **Title:** SYNTHESIS OF DIMETHYL CARBONATE AND RELATED COMPOUNDS

(57) **Abstract:** An improved process for synthesis of dimethyl carabonate (DMC) and related compounds further, starting from urea or methyl carbamate and methanol employing novel catalysts, double metal cyanides, cenospheres, hydrotalcites and hydrotalcite like compunds.



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“SYNTHESIS OF DIMETHYL CARBONATE AND RELATED COMPOUNDS”

The following specification particularly describes the invention and the manner in which it is to be performed:

TECHNICAL FIELD OF THE INVENTION

Present invention relates to the synthesis of dimethyl carbonate (DMC) and related compounds further, starting from urea or methyl carbamate and methanol employing catalysts selected from the group consisting of double metal cyanides, cenospheres, hydrotalcites and hydrotalcite like compounds.

BACKGROUND AND PRIOR ART OF THE INVENTION

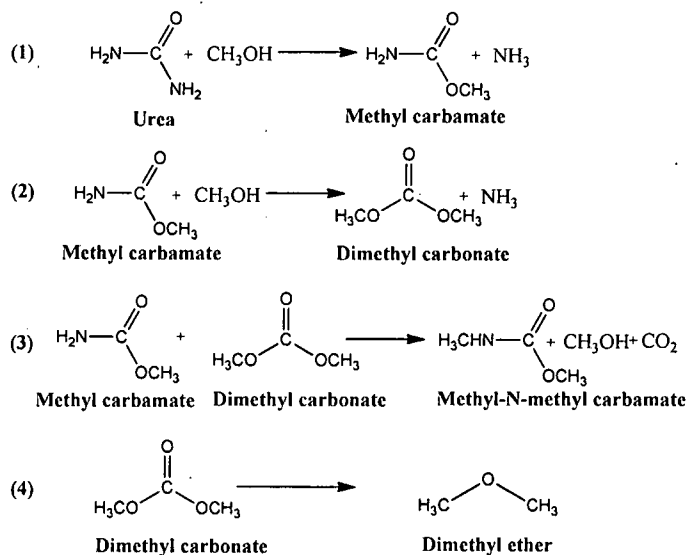
Dimethyl carbonate (DMC) is an important intermediate and is widely used in industry. Owing to its low toxicity, dimethyl carbonate is considered a "green" chemical product with bright development prospects. DMC is a versatile chemical and has been used mainly as a methylating and methoxy carbonylating agent as a safe substitute for dimethyl sulphate, phosgene or methyl halide, which are toxic or corrosive. It can also be used as a solvent to replace halogenated solvents. DMC has a high octane number and could be a good additive for gasoline in the future and could lead to increase in demand of DMC. This increasing focus on the use of DMC is mainly due to the bio-degradability, with a low bioaccumulation as well as its low toxicity.

Presently, DMC is produced mainly from methanol and phosgene in concentrated NaOH solution. Because of the use of phosgene for its production, DMC has been limited in industrial use. DMC also can be produced by non-phosgene route which includes oxidative carbonylation of methanol in liquid phase, which was put on stream in the EniChem Ravenna factory using CuCl catalyst. The major drawbacks of this process are low production rate; high cost of separation of products and reactants, high recycle requirements and the need for corrosion resistant reactor and process lines. Another non-phosgene process was the synthesis of DMC by trans esterification of cyclic carbonate with methanol developed by Asahi Kasei Chemical, Japan. The main disadvantages of the route are: the slow reaction rate of epoxides with CO₂ and requirement of high pressures, and the exchange reaction of the cyclic carbonate with methanol are limited by equilibrium. The economy of the process is affected due to the use of epoxide which is expensive and formation of ethylene glycol as a by-product in stoichiometric quantity. CO₂ as a readily available, inexpensive and environmentally acceptable material has been widely investigated as raw material for DMC synthesis. But still the progress made so far

is not satisfactory due to the difficulty of activation of CO₂, and thermodynamic limitations.

Synthesis of DMC by the reaction of urea and methanol is an attractive alternative route. This will be a GREEN Process, being based on cheap and renewable raw materials.

5 The reaction scheme is presented below:



Scheme 1

There are several patents (Refer EP1777212, US4436668) as well as publications in recent times on the synthesis of DMC from methanol and urea leading to the development of new and improved catalysts and methodologies for this important reaction. Reaction of urea with methanol gives methyl carbamate (MC) as an intermediate (Scheme 1). The second step of converting MC to DMC is more difficult than the first step and is an equilibrium controlled reaction. This is because the ammonia produced in the reaction can restrict the progress of the reaction. Efficient removal of by-product ammonia and product DMC is necessary to shift the equilibrium and increase the yield of DMC.

Several catalyst systems have been tried for making the process of synthesis of DMC more efficient in terms of selectivity towards desired product, increased conversion and other parameters.

Cenospheres are used as efficient catalysts in oxidative coupling and deep oxidation of methane (Refer: Article titled "**Microspheres of Fly ash as a source for catalytic supports, adsorbents and catalysts**" by S.N. Vereshchagan et al. in chemistry for sustainable development 11(2003) 303-308, Article titled "**TiO₂-Coated Cenospheres as Catalysts for Photocatalytic Degradation of Methylene Blue, *p*-Nitroaniline, *n*-Decane, and *n*-Tridecane under Solar Irradiation**" by Praveen K. Surolia, Rajesh J. Tayade et.al in Ind. Eng. Chem. Res., 2010, 49 (19), pp 8908-8919).

US 7,888,409 discloses to an aromatic polycarbonate resin composition comprising 100 parts by mass of an aromatic polycarbonate resin (A) and 0.1 to 50 parts by mass of cenosphere (B). Further comprising 100 parts by mass or less of a styrene resin and/ or a polyester resin (C). But the use of cenospheres for the synthesis of DMC is hitherto unexplored.

Hydrotalcites have been explored as catalysts for synthesis of DMC. An Article titled "Synthesis of dimethyl carbonate from methyl carbamate and methanol catalyzed by mixed oxides from hydrotalcite-like compounds" by Wang et al. in Journal of Physics and Chemistry of Solids 71 (2010) 427-430 discloses preparation and study of a series of mixed oxides calcined from hydrotalcite-like compounds with different cations for the synthesis of dimethyl carbonate (DMC) from methyl carbamate(MC) and methanol. It also discloses layered double hydrotalcites (LDHs) or anionic clays with a divalent metal cation or trivalent metal cation. But the selectivity of these catalysts towards DMC is in the range of 3-32%.

WO2011013880 provides a method for preparing dialkyl carbonate from urea or alkyl carbamate and alkyl alcohol using an ionic liquid comprising a cation, which produces a hydrogen ion (H^+), and a hydrophobic anion containing fluorine and a catalyst containing at least one selected from the group consisting of an alkali earth metal oxide, a transition metal oxide, a rare earth oxide, and a hydrotalcite.

The catalyst may be at least one selected from the group consisting of an alkali earth metal oxide, a transition metal oxide, a rare earth oxide which may be impregnated onto a support such as silica, alumina, titania, zirconia or ceria, wherein the alkali earth metal oxide, the transition metal oxide, the rare earth oxide include CaO , MgO , ZnO , CuO , PbO , La_2O_3 , Y_2O_3 which can be impregnated onto a support. Further, the catalyst may be a mixed oxide with a crystalline composite oxide such as hydrotalcite. Although the size of the catalyst is not particularly limited, the reaction rate is increased and the yield is improved when a nano-sized catalyst is used.

However, the patent talks of the use of Mg/Al hydrotalcite as the catalyst and other hydrotalcite materials are not covered by the patent. Another limitation is the amount of hydrotalcite as catalyst which cannot exceed above 10 parts by weight. The patent claims the amount of catalyst used is preferably 1 to 10 parts by weight of the ionic liquid. If the amount of hydrotalcite exceeds above 10 parts by weight, the yield improvement effect by an increase in the amount of catalyst used is reduced due to an increase in viscosity, which is uneconomic.

OBJECTS OF THE INVENTION

Main object of the present invention is synthesis of dimethyl carbonate (DMC) and related compounds further, starting from urea or methyl carbamate and methanol employing catalysts selected from the group consisting of double metal cyanides, cenospheres, hydrotalcites and hydrotalcite like compounds.

Another object of the present invention is to provide an efficient process for the synthesis of dimethyl carbonate (DMC) and further Methyl-N-methyl carbamate (MNMC) and dimethyl ether (DME).

Yet another object of the present invention is to provide a process of synthesis of DMC and further MNMC and DME catalysed by hydrotalcites and hydrotalcite like compounds, double metal cyanides and cenospheres.

SUMMARY OF INVENTION

Accordingly, present invention provides a process for the preparation of di methyl carbonate (DMC) using catalyst selected from the group consisting of double metal cyanides, cenosphere and hydrotalcites of divalent or trivalent metals catalysts and the said process comprises charging urea or methyl carbamate and methanol in the range of 1:1 to 1:20, preferably 1:5 to 1:17 with the catalyst in a high pressure reactor followed by heating at temperature in the range of 100-300°C, preferably 140-200°C with stirring for period in the range of 5-10 hours with continuously removing ammonia from the reactor to obtain di methyl carbonate (DMC).

In an embodiment of the present invention, conversion percentage of urea is in the range of 80 to 99%.

In another embodiment of the present invention, conversion of methyl carbamate is in the range of 1-99%.

In yet another embodiment of the present invention, the selectivity of the process towards DMC is in the range of 1-90%.

In yet another embodiment of the present invention, the said process further synthesizes MNMC from DZMC with selectivity of the process towards MNMC is in the range of 1-10%.

In yet another embodiment of the present invention, the catalyst cenospheres and double metal cyanide catalyst used is optionally activated.

In yet another embodiment of the present invention, the cenospheres are impregnated with metal selected from the group consisting of cobalt, iron, copper, sodium, potassium and zinc.

In yet another embodiment of the present invention, divalent metals are alkaline earth metals are selected from Mg, Ca, Sr, and Ba and transition metals are selected from Mn,

Zr, Ni, Co, Cu and Zn or trivalent metals are selected from Al, Ga, Cr, Mn, Fe, Co, La, Ce, Sm and Nd.

In yet another embodiment of the present invention, the catalyst used is either unsupported or supported.

- 5 In yet another embodiment of the present invention, the double metal cyanide catalyst is prepared from metals selected from Ca, Fe, Zn, Co, Cu, Sn, Mg, Ni, Ce, Nd, Ba, Sr, Ce and La.

In yet another embodiment of the present invention, the double metal cyanide catalyst is complexed with agents selected from polyethylene glycol, β -cyclodextrin, tween-60, tert-butanol, 1,2-dimethoxyethane, 2-methoxy ethanol, 1-methyl-2-propanol, 1,2-propanediol, tetrahydrofuran, 1,4-dioxane, hexamethylenetetramine, lactate esters with alkyl alcohols and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly (ethylene glycol) .

In yet another embodiment of the present invention, catalyst loading is in the range of 0.01 to 10 weight % based on urea or methyl carbamate used as a reactant.

- 15 In yet another embodiment of the present invention, said process further synthesizes methy-N-methyl carbamate.

ABBREVIATIONS USED

DMC: Di methyl carbonate

MC: Methyl carbamate

- 20 MNMC: Methyl-N-Methyl carbamate

DME: Di methyl ether

DETAILED DESCRIPTION OF INVENTION

Present invention provides a process for the synthesis of dimethyl carbonate (DMC) and related compounds further, starting from urea or methyl carbamate and methanol employing novel catalyst, double metal cyanides, cenospheres, hydrotalcites.

25 Dimethyl carbonate formed as a product reacts with methyl carbamate to obtain Methyl-N-methyl carbamate (MNMC). DMC can also be used for the further synthesis of DME.

Double metal cyanide catalysts are prepared by reacting a water soluble metal salt, a water soluble metal cyanide salt, an electron donating complexing agent and water. The soluble metals salt is selected from di and tri valent metals. The divalent metals used include Sn, alkaline earth metal salts of Mg, Ca, Sr, Ba, transition metal like Fe, Zn, Co, Cu, Ni, Zr and tri valent metals used include Fe, La, Ce, Nd, Sm, Co etc. The complexing agents are selected from polyethylene glycol, β -cyclodextrin, tween-60, tert-butanol, 1,2-dimethoxyethane, 2-methoxy ethanol, 1-methyl-2-propanol, 1,2-propanediol, tetrahydrofuran, 1,4-dioxane, hexamethylenetetramine, lactate esters with alkyl alcohols and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly (ethylene glycol) .

The catalyst $\text{Zn}_2\text{Fe}(\text{CN})_6$ was prepared as per the literature procedure (Y. Fang, Y. Zhen-hong, L. Peng-Mai, L. Wen, Y. Ling-Mai, D. Li Journal of Fuel Chemistry and Technology 38(3), (2010) 281 and R. Srivastava, D. Srinivas, P. Ratnasamy Journal of Catalysis 241 (2006) 34).

- 5 The catalyst $\text{LaFe}(\text{CN})_6$ was prepared by modified procedure with regard to the reference provided herein.

Cenospheres are light weight, unique free flowing powders composed of hard shelled, hollow spheres comprised largely of silica, alumina, iron, sodium and potassium. Cenospheres also comprise of calcium, magnesium, zinc, manganese and such like in
10 small concentrations. Cenospheres are hollow ceramic microspheres found in fly ash, a natural by-product of coal combustion during the generation of electric power. Cenospheres have a size range from 1 to 500 microns with an average compressive strength of 3000+ psi. Their colors range from white to dark gray. They are also referred to as microspheres, hollow spheres, hollow ceramic microspheres, microballoons, or glass
15 beads. The microspheres reveal thermal, magnetic and some other properties like low specific gravity, spherical shape, controlled size, high compression and chemical inertness.

Cenospheres comprising of silica, alumina, iron, sodium, potassium, zinc and such like are employed as catalyst for DMC synthesis. The activity and DMC selectivity may be
20 tailored by modification of cenospheres by various methods such as steam treatment, by tailoring acid-base properties with doping of alkali, alkaline and rare earth metals and activation at high temperatures.

The catalysts of the invention are selected from clays such as hydrotalcites, sepiolites either alone or in combinations thereof. Hydrotalcites are prepared from divalent and
25 trivalent metals. In the present invention, hydrotalcite contain combination of divalent or trivalent metals to give binary, ternary hydrotalcites. The divalent metals to be used include: alkaline earth metals (Mg, Ca, Sr, Ba) transition metals (Mn, Zr, Ni, Co, Cu and Zn). The trivalent metals to be used include: Al, Ga, Cr, Mn, Fe, Co, La, Ce, Sm, Nd and such like.

- 30 In an aspect of the invention, the catalyst for the process of the invention is prepared by a process comprising:

- a. mixing solution A comprising of metal nitrates with solution B comprising of alkali in distilled water;
- b. adding the solutions drop wise to water to cause precipitation by maintaining pH
35 between 9-10;
- c. aging the precipitate in mother liquor under stirring;

- d. filtering and washing the precipitate with distilled water till pH 7 was obtained to get rid of alkali and NO_3^- ions.
- e. Drying the precipitate and crushing to a fine powder and
- f. Calcining the powder under N_2 flow.

5 The catalyst used is either supported or used without support.

The process of the invention comprises the steps of:

- a) charging urea or methyl carbamate and methanol in the range of 1:1 to 1:20, preferably 1:5 to 1:17 with the catalyst in a high pressure reactor and heating to 100-300°C, preferably 150-200°C with stirring for 5-10 hours;
- 10 b) continuously removing ammonia from the reactor and;
- c) cooling the mixture of step (a) to 20-35°C to obtain the desired products.

The step of reacting methanol with urea to obtain methyl carbamate proceeds without a catalyst. The step of reacting methanol with urea to obtain methyl carbamate proceeds in the presence of catalyst known in the art.

- 15 The step of reacting methanol with urea or methyl carbamate to obtain dimethyl carbonate proceeds in the presence of double metal cyanide, cenospheres and hydrotalcites or hydrotalcite like compounds, sepiolites and hydroxypetite clays as catalysts of the invention.

The process of urea reacting with methanol to provide DMC is a one pot process.

- 20 The step of reacting methanol with urea or methyl carbamate to dimethyl carbonate proceeds in the presence of cenospheres or modified cenospheres as catalysts of the invention.

EXAMPLES

- 25 Following examples are given by way of illustration and therefore should not be construed to limit the scope of the invention.

COMPARATIVE EXAMPLES 1 TO 7 FOR THE SYNTHESIS OF DOUBLE METAL CYANIDE COMPLEXES

- Various double metal cyanide complexes like $\text{Zn}_2\text{Fe}(\text{CN})_6$, $\text{La}_4[\text{Fe}(\text{CN})_6]_3$, $\text{Cu}_3[\text{Co}(\text{CN})_6]_2$, $\text{Cu}_2\text{Fe}(\text{CN})_6$, $\text{Zn}_3[\text{Co}(\text{CN})_6]_2$, were synthesized by using the procedure reported by Y. Fang, Y. Zhen-hong, L. Peng-Mai, L. Wen, Y. Ling-Mai, D. Li Journal of Fuel Chemistry and Technology 38(3), (2010) 281.

COMPARATIVE EXAMPLE 1

Synthesis of $\text{Zn}_2\text{Fe}(\text{CN})_6$

- 35 Solution 1 was prepared by dissolving 0.01mole of potassium ferrocyanide in 40 ml distilled water while solution 2 was prepared by dissolving 0.1 mole of ZnCl_2 in 18 ml distilled water and 20 ml t-Butanol. Solution 2 was added to solution 1 with constant

stirring over a period of 1 hour at 323K. Resultant solid was isolated and washed with distilled water to remove any uncomplexed ions and dried overnight at 333K.

COMPARATIVE EXAMPLE 2

Synthesis of $\text{La}_4[\text{Fe}(\text{CN})_6]_3$

- 5 Solution A was prepared by dissolving 3.68 gm (0.01M) of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ in 40 ml DI water. Solution B was prepared by dissolving 37.1 gm LaCl_3 (0.1M) in mixture of 18 ml DI water and 20 ml tert-butanol. 15 gm tri-block copolymer, poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ average molecular weight=5800) was dissolved in 2 ml distilled water and 40 ml tert-butanol to prepare
10 solution C. Solution A and C were slowly added to solution B over a period of 1 hrs at 50°C with constant stirring. Stirring was continued for 1 more hour. White precipitate thus obtained was isolated by filtration washed repeatedly with DI water and dried at 50°C for 15 hrs. La-Fe Double metal cyanide was activated at 180°C before use.

COMPARATIVE EXAMPLE 3

15 Synthesis of $\text{Sn}_2\text{Fe}(\text{CN})_6$

- 7.36 gm $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ was dissolved in 80 ml 1 M hydrochloric acid. To this solution, a solution of 18 gm SnCl_2 in 80 ml DI 2M HCl was added over a period of 1 hr at room temperature with constant stirring. Resultant white precipitate was aged overnight at room temperature. During aging colour of precipitate changed from white to dark blue.
20 This blue solid was then isolated by filtration washed repeatedly till free from acid and dried at 50°C for 15 hrs. Sn-Fe(II) DMC was used without activation.

COMPARATIVE EXAMPLE 4

Synthesis of Ca modified $\text{Zn}_2\text{Fe}(\text{CN})_6$

- A aqueous solution of 3gm (0.0081M) $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ in 80ml distilled H_2O was added
25 drop wise to a solution containing 10 gm (0.073M) ZnCl_2 and 0.1 gm (0.0001M) CaCl_2 in 50 ml distilled water and 10 ml tertiary butanol at 50°C . Solution was stirred continuously during addition. White precipitate obtained after addition was isolated by filtration and resuspended in 1:1 tertiary butanol water mixture. Filtration and resuspension process was repeated 5 times then precipitate was washed with 1000 ml distilled water and dried
30 at 50°C for 15 hrs.

COMPARATIVE EXAMPLE 5

Synthesis of $\text{Zn}_3[\text{Co}(\text{CN})_6]_2$

- Solution A was prepared by dissolving 3.32 gm (0.01M) of $\text{K}_3[\text{Co}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ in 40 ml DI water. Solution B was prepared by dissolving 17.4gm ZnCl_2 (0.1M) in mixture of 18 ml DI
35 water and 20 ml tert-butanol. 15 gm tri-block copolymer, poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ average molecular

weight=5800) was dissolved in 2 ml distilled water and 40 ml tert-butanol to prepare solution C. Solution A and C were slowly added to solution B over a period of 1 hrs at 50°C with constant stirring, Stirring was continued for 1 more hour. Sky blue precipitate thus obtained was isolated by filtration washed repeatedly with DI water and dried at 50°C for 15 hrs. Co-Zn(II) Double Metal Cyanide was activated at 180°C before use.

COMPARATIVE EXAMPLE 6

Synthesis of $\text{Cu}_2\text{Fe}(\text{CN})_6$

Solution A was prepared by dissolving 3.68 gm (0.01M) of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ in 40 ml DI water. Solution B was prepared by dissolving 17.4 gm CuCl_2 (0.1M) in mixture of 18 ml DI water and 20 ml tert-butanol. 15 gm tri-block copolymer, poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ average molecular weight=5800) was dissolved in 2 ml distilled water and 40 ml tert-butanol to prepare solution C. Solution A and C were slowly added to solution B over a period of 1 hrs at 50°C with constant stirring, Stirring was continued for 1 more hour. White precipitate thus obtained was isolated by filtration washed repeatedly with DI water and dried at 50°C for 15 hrs. Cu-Fe(II) Double Metal cyanide was activated at 180°C before use.

COMPARATIVE EXAMPLE 7

Synthesis of $\text{Zn}_3[\text{Fe}(\text{III})(\text{CN})_6]_2$

Solution A was prepared by dissolving 3.29 gm (0.01M) of $\text{K}_3[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ in 40 ml DI water. Solution B was prepared by dissolving 13.63 gm ZnCl_2 (0.1M) in mixture of 18 ml DI water and 20 ml tert-butanol. 15 gm tri-block copolymer, poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ average molecular weight=5800) was dissolved in 2 ml distilled water and 40 ml tert-butanol to prepare solution C. Solution A and C were slowly added to solution B over a period of 1 hrs at 50°C with constant stirring, Stirring was continued for 1 more hour. White precipitate thus obtained was isolated by filtration washed repeatedly with DI water and dried at 50°C for 15 hrs. Zn-Fe(II) Double metal cyanide was activated at 180°C to get blue solid.

COMPARATIVE EXAMPLES 8 TO 13 FOR THE SYNTHESIS OF CENOSPHERES

Various metal oxides impregnated on censpheres were synthesized by using procedure reported

- i. O. Babajide, L. Petrik, N. Musyoka, B. Amigun, F. Ameer, *Petroluem and Coal*, 52,4,2010,261.
- ii. Z. Aixiang, X. Weihao, W. Caifang, Z. Qionghua, *Journal of Wuhan University of Technology-Mater.Sci.Ed.*, 21,3, 2006, 129.
- iii. D. Jain, C. Khatri, A. Rani., *Fuel*, 90,2011,2083.

COMPARATIVE EXAMPLE 8**Preparation of KNO₃ impregnated on cenosphere**

The thin layer of KNO₃ deposited on cenosphere were prepared by thermal decomposition of potassium nitrate on the support surface, including the impregnation of cenosphere (5gm) with ethanolic potassium nitrate solution of (0.5gm per 10 ml of ethanol) given concentration & drying at 110°C for 12 h followed by calcination of the sample at 500°C for 2 hrs & 600°C for 6 hrs.

COMPARATIVE EXAMPLE 9**Preparation of Fe₂O₃ impregnated on cenosphere**

The thin layer of iron oxide deposited on cenosphere were prepared by thermal decomposition of Iron nitrate on the support surface, including the impregnation of cenosphere(5gm) with ethanolic Iron nitrate solution of (0.5 gm per 10 ml of ethanol) given concentration & drying at 110°C for 12 h followed by calcination of the sample at 500°C for 2 hrs & 600°C for 6 hrs.

COMPARATIVE EXAMPLE 10**Preparation of CuO impregnated on cenosphere**

The thin layer of copper oxide deposited on cenosphere were prepared by thermal decomposition of cupric nitrate on the support surface, including the impregnation of cenosphere(5 gm) with ethanolic cupric nitrate solution of (0.5 gm per 10 ml of ethanol) given concentration & drying at 110°C for 12 h followed by calcination of the sample at 500°C for 2 hrs & 600°C for 6 hrs.

COMPARATIVE EXAMPLE 11**Preparation of CoO impregnated on cenosphere**

The thin layer of cobalt oxide deposited on cenosphere were prepared by thermal decomposition of cobalt nitrate on the support surface, including the impregnation of cenosphere (5 gm) with ethanolic cobalt nitrate solution of (0.5 gm per 10 ml of ethanol) given concentration & drying at 110°C for 12 h followed by calcination of the sample at 500°C for 2 hrs & 600°C for 6 hrs.

COMPARATIVE EXAMPLE 12**Synthesis of BaFe₁₂O₁₉ coated on cenosphere by Sol-Gel method**

Preparation of gel was done by combination of 0.05 M barium nitrate (0.6533 g) & Iron nitrate (11.11 g) with aqueous solution of citric acid (10.567 g). Composition ratio of barium nitrate & Iron nitrate was 1:11 respectively. The solution was refluxed at 70°C for 24 hrs. After the resulting precursor solution was made, a total 5 g of cenosphere were stirred in the precursor solution for 3hrs. The resulting precursor was filter off & dried at 450° C for 2 hrs followed by calcination at 850°C for 2 hrs.

COMPARATIVE EXAMPLE 13**Synthesis of chemical activated cenosphere**

Chemical activation of cenospheres was done by heating cenospheres with NaOH 50 weight % at 110°C in round bottom flask equipped with condenser under vigorous stirring. The activation was continued for 1 day followed by ageing for 1 day. The obtained pulp was washed with distilled water to remove leached compounds and excess alkali. This catalyst was calcined at 450°C for 4 h.

COMPARATIVE EXAMPLES 14 to 22 FOR THE SYNTHESIS OF HYDROTALCITES AND HYDROTALCITE LIKE MATERIALS

Hydrotalcites and hydrotalcite like materials were prepared by co-precipitation from their nitrate precursors in alkaline medium as per the procedure reported by Al-Esaimi et al. (M. M. Al-Esaimi, International Journal of Polymeric Materials, 2000, Vol. 45. pp. 55 – 68).

COMPARATIVE EXAMPLE 14

Preparation of CaAlHTlc , ($x=3$, wherein 'x' is molar ratio of divalent to trivalent metals)

Ca-Al hydrotalcite like clays with $\text{Ca}^{2+}/\text{Al}^{3+}$ ratio of 3 was prepared by mixing solution A comprising of metal nitrates with solution B comprising of alkali. Solution A was prepared by dissolving 0.06M $\text{Ca}(\text{NO}_3)_2$ and 0.02M $\text{Al}(\text{NO}_3)_3$ in 100 ml distilled water. Similarly solution B was prepared by dissolving 0.086M Na_2CO_3 and 0.03M NaOH in 70 ml distilled water. The precipitation was carried out by drop wise addition of both solutions into a beaker containing 100ml distilled water at 60°C under stirring condition. During addition pH was maintained between 9-10 by controlled addition of solution B for 2 hours. After completion of addition of both the solutions, a white precipitate appears with the final pH 11. This precipitate was then kept for aging in mother liquor under stirring condition at 60°C for 3h. This was followed by filtration and washing of the precipitate with distilled water till pH 7 was obtained to get rid of Na^+ and NO_3^- ions. The alkali free precipitate was dried at 80 °C for 12h and crushed to fine powder. The calcined hydrotalcite was obtained by calcining this powder at 550°C for 5h under N_2 flow.

COMPARATIVE EXAMPLE 15

Preparation of CaFeHTlc ($x=3$)

For preparing Ca-Fe hydrotalcite with $\text{Ca}^{2+}/\text{Fe}^{3+}$ ratio of 3, solution A comprising of metal nitrates was mixed with solution B comprising of alkali. Solution A was prepared by dissolving 0.06M $\text{Ca}(\text{NO}_3)_2$ and 0.02M $\text{Fe}(\text{NO}_3)_3$ in 100 ml distilled water. Similarly solution B was prepared by dissolving 0.086M Na_2CO_3 and 0.03M NaOH in 70 ml distilled water. The precipitation was carried out by drop wise addition of both solutions into a

beaker containing 100ml distilled water at 60°C under stirring condition. During addition pH was maintained between 9-10 by controlled addition of solution B for 2 hours. After completion of addition of both the solutions, a brown precipitate appears with the final pH 11. This precipitate was then kept for aging in mother liquor under stirring condition at 60°C for 3h. This was followed by filtration and washing of the precipitate with distilled water till pH 7 was obtained to get rid of Na^+ and NO_3^- ions. The alkali free precipitate was dried at 80 °C for 12h and crushed to fine powder. The calcined hydrotalcite was obtained by calcining this powder at 550°C for 5h under N_2 flow.

COMPARATIVE EXAMPLE 16

Preparation of CoLaHTlc, Co-La hydrotalcite with $\text{Co}^{2+}/\text{La}^{3+}$ ratio of 2 was prepared by mixing solution A comprising of metal nitrates and solution B comprising of alkali. Solution A was prepared by dissolving 0.067M $\text{Co}(\text{NO}_3)_2$ and 0.033M $\text{La}(\text{NO}_3)_3$ in 100 ml distilled water. Similarly solution B was prepared by dissolving 0.15M Na_2CO_3 and 0.068M NaOH in 100 ml distilled water. The precipitation was carried out by drop wise addition of both solutions into a beaker containing 100ml distilled water at 60°C under stirring condition. During addition pH was maintained between 9-10 by controlled addition of solution B for 2 hours. After completion of addition of both the solutions, a blue precipitate appears with the final pH 11. This precipitate was then kept for aging in mother liquor under stirring condition at 60°C for 3h. This was followed by filtration and washing of the precipitate with distilled water till pH 7 was obtained to get rid of Na^+ and NO_3^- ions. The alkali free precipitate was dried at 80 °C for 12h and crushed to fine powder. The calcined hydrotalcite was obtained by calcining this powder at 550 °C for 5h under N_2 flow. Similar procedure was followed for preparation of ZnLaHTlc ($x=2$), LaFeHTlc ($x=2$), FeMnHTlc ($x=2$), CeMnHTlc ($x=2$), CeCoHTlc ($x=2$).

COMPARATIVE EXAMPLE 17

Preparation of SrAlHTlc ($x=3$)

Sr-Al hydrotalcite like clays with $\text{Sr}^{2+}/\text{Al}^{3+}$ ratio of 3 was prepared by mixing solution A comprising of metal nitrates with solution B comprising of alkali. Solution A was prepared by dissolving 0.06 M $\text{Sr}(\text{NO}_3)_2$ and 0.02M $\text{Al}(\text{NO}_3)_3$ in 100 ml distilled water. Similarly solution B was prepared by dissolving 0.086M Na_2CO_3 and 0.03M NaOH in 70 ml distilled water. The precipitation was carried out by drop wise addition of both solutions into a beaker containing 100ml distilled water at 60°C under stirring condition. During addition pH was maintained between 9-10 by controlled addition of solution B for 2 hours. After completion of addition of both the solutions, a white precipitate appears with the final pH 11. This precipitate was then kept for aging in mother liquor under stirring condition at 60°C for 3h. This was followed by filtration and washing of the precipitate with distilled

water till pH 7 was obtained to get rid of Na^+ and NO_3^- ions. The alkali free precipitate was dried at 80 °C for 12h and crushed to fine powder. The calcined hydrotalcite was obtained by calcining this powder at 550 °C for 5h under N_2 flow.

COMPARATIVE EXAMPLE 18

5 Zn-La hydrotalcite with $\text{Zn}^{2+}/\text{La}^{3+}$ ratio of 2 was prepared by mixing solution A comprising of metal nitrates and solution B comprising of alkali. Solution A was prepared by dissolving 0.266M $\text{Zn}(\text{NO}_3)_2$ and 0.133M $\text{La}(\text{NO}_3)_3$ in 100 ml distilled water. Similarly solution B was prepared by dissolving 0.15M Na_2CO_3 and 0.068M NaOH in 100 ml distilled water. The precipitation was carried out by drop wise addition of both solutions
10 into a beaker containing 100ml distilled water at 60°C under stirring condition. During addition pH was maintained between 9-10 by controlled addition of solution B for 2 hours. After completion of addition of both the solutions, a blue precipitate appears with the final pH 11. This precipitate was then kept for aging in mother liquor under stirring condition at 60°C for 3h. This was followed by filtration and washing of the precipitate
15 with distilled water till pH 7 was obtained to get rid of Na^+ and NO_3^- ions. The alkali free precipitate was dried at 80 °C for 12h and crushed to fine powder. The calcined hydrotalcite was obtained by calcining this powder at 550 °C for 5h under N_2 flow.

COMPARATIVE EXAMPLE 19

Fe-La hydrotalcite with $\text{Fe}^{2+}/\text{La}^{3+}$ ratio of 2 was prepared by mixing solution A comprising
20 of metal nitrates and solution B comprising of alkali. Solution A was prepared by dissolving 0.267M FeCl_2 and 0.133M $\text{La}(\text{NO}_3)_3$ in 100 ml distilled water. Similarly solution B was prepared by dissolving 0.15M Na_2CO_3 and 0.068M NaOH in 100 ml distilled water. The precipitation was carried out by drop wise addition of both solutions into a beaker containing 100ml distilled water at 60°C under stirring condition. During
25 addition pH was maintained between 9-10 by controlled addition of solution B for 2 hours. After completion of addition of both the solutions, a brownish green precipitate appears with the final pH 11. This precipitate was then kept for aging in mother liquor under stirring condition at 60°C for 3h. This was followed by filtration and washing of the precipitate with distilled water till pH 7 was obtained to get rid of Na^+ and NO_3^- ions. The
30 alkali free precipitate was dried at 80 °C for 12h and crushed to fine powder. The calcined hydrotalcite was obtained by calcining this powder at 550 °C for 5h under N_2 flow.

COMPARATIVE EXAMPLE 20

Fe-Mn hydrotalcite with $\text{Fe}^{2+}/\text{Mn}^{3+}$ ratio of 2 was prepared by mixing solution A comprising of metal nitrates and solution B comprising of alkali. Solution A was prepared
35 by dissolving 0.267M $\text{Mn}(\text{NO}_3)_2$ and 0.133M $\text{Fe}(\text{NO}_3)_3$ in 100 ml distilled water. Similarly solution B was prepared by dissolving 0.15M Na_2CO_3 and 0.068M NaOH in 100 ml

distilled water. The precipitation was carried out by drop wise addition of both solutions into a beaker containing 100ml distilled water at 60°C under stirring condition. During addition pH was maintained between 9-10 by controlled addition of solution B for 2 hours. After completion of addition of both the solutions, a brown precipitate appears with the final pH 11. This precipitate was then kept for aging in mother liquor under stirring condition at 60°C for 3h. This was followed by filtration and washing of the precipitate with distilled water till pH 7 was obtained to get rid of Na⁺ and NO₃⁻ ions. The alkali free precipitate was dried at 80 °C for 12h and crushed to fine powder. The calcined hydrotalcite was obtained by calcining this powder at 550 °C for 5h under N₂ flow.

COMPARATIVE EXAMPLE 21

Ce-Mn hydrotalcite with Ce²⁺/Mn³⁺ ratio of 2 was prepared by mixing solution A comprising of metal nitrates and solution B comprising of alkali. Solution A was prepared by dissolving 0.267M Mn(NO₃)₂ and 0.133M Ce(NO₃)₃ in 100 ml distilled water. Similarly solution B was prepared by dissolving 0.15M Na₂CO₃ and 0.068M NaOH in 100 ml distilled water. The precipitation was carried out by drop wise addition of both solutions into a beaker containing 100ml distilled water at 60°C under stirring condition. During addition pH was maintained between 9-10 by controlled addition of solution B for 2 hours. After completion of addition of both the solutions, a dark brown precipitate appears with the final pH 11. This precipitate was then kept for aging in mother liquor under stirring condition at 60°C for 3h. This was followed by filtration and washing of the precipitate with distilled water till pH 7 was obtained to get rid of Na⁺ and NO₃⁻ ions. The alkali free precipitate was dried at 80 °C for 12h and crushed to fine powder. The calcined hydrotalcite was obtained by calcining this powder at 550 °C for 5h under N₂ flow.

COMPARATIVE EXAMPLE 22

Ce-Co hydrotalcite with Ce²⁺/Co³⁺ ratio of 2 was prepared by mixing solution A comprising of metal nitrates and solution B comprising of alkali. Solution A was prepared by dissolving 0.267M Co(NO₃)₂ and 0.133M Ce(NO₃)₃ in 100 ml distilled water. Similarly solution B was prepared by dissolving 0.15M Na₂CO₃ and 0.068M NaOH in 100 ml distilled water. The precipitation was carried out by drop wise addition of both solutions into a beaker containing 100ml distilled water at 60°C under stirring condition. During addition pH was maintained between 9-10 by controlled addition of solution B for 2 hours. After completion of addition of both the solutions, a bluish green precipitate appears with the final pH 11. This precipitate was then kept for aging in mother liquor under stirring condition at 60°C for 3h. This was followed by filtration and washing of the precipitate with distilled water till pH 7 was obtained to get rid of Na⁺ and NO₃⁻ ions. The

alkali free precipitate was dried at 80 °C for 12h and crushed to fine powder. The calcined hydrotalcite was obtained by calcining this powder at 550 °C for 5h under N₂ flow.

EXAMPLS 1 TO 10 FOR THE PREPARATION OF DMC USING DOUBLE METAL CYANIDE CATALYSTS

Example 1

Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1g of Zn₂Fe(CN)₆ were charged to a 300 ml reactor. The contents were heated to 180 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 27.1% conversion of methyl carbamate with 12.8% selectivity to dimethyl carbonate was observed in the reaction. Product has been characterized by GCMS.

Example 2

Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1g of LaFe(CN)₆ were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 16.1% conversion of methyl carbamate with 8.3% selectivity to dimethyl carbonate and 3.8% selectivity to methyl N-methyl carbamate was observed in the reaction.

Example 3

Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1g of SnFe(CN)₆ were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 11.9%

conversion of methyl carbamate with 12.7% selectivity to dimethyl carbonate and 1% selectivity to methyl N-methyl carbamate was observed in the reaction.

Example 4

Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1g of CaFe(CN)₆ were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 47% conversion of methyl carbamate with 4.1% selectivity to dimethyl carbonate and 6.2% selectivity to methyl N-methyl carbamate was observed in the reaction.

Example 5

Urea 7.5 g (125 mmol), methanol 65 g (2030 mmol) and 1g of CuCo(CN)₆ were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 99% conversion of urea with 61.3% selectivity to methyl carbamate, 0.30% selectivity to dimethyl carbonate and 4.2% selectivity to methyl N-methyl carbamate was observed in the reaction.

Example 6

Urea 7.5 g (125 mmol), methanol 65 g (2030 mmol) and 1g of CuFe(CN)₆ were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 99.2% conversion of urea with 63.7% selectivity to methyl carbamate, 0.41% selectivity to dimethyl carbonate and 4.6% selectivity to methyl N-methyl carbamate was observed in the reaction.

Example 7

Urea 7.5 g (125 mmol), methanol 65 g (2030 mmol) and 1g of $\text{ZnFe}(\text{CN})_6$ were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 95.7% conversion of urea with 44.3% selectivity to methyl carbamate, 0.76% selectivity to dimethyl carbonate and 7% selectivity to methyl N-methyl carbamate was observed in the reaction.

Example 8

Urea 7.5 g (125 mmol), methanol 65 g (2030 mmol) and 1g of $\text{LaFe}(\text{CN})_6$ were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 99.4% conversion of urea with 54.4% selectivity to methyl carbamate, 0.96% selectivity to dimethyl carbonate and 8.1% selectivity to methyl N-methyl carbamate was observed in the reaction.

Example 9

Urea 7.5 g (125 mmol), methanol 65 g (2030 mmol) and 1g of $\text{SnFe}(\text{CN})_6$ were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 95.2% conversion of urea with 54.3% selectivity to methyl carbamate, 0.78% selectivity to dimethyl carbonate and 6.1% selectivity to methyl N-methyl carbamate was observed in the reaction.

Example 10

Urea 7.5 g (125 mmol), methanol 65 g (2030 mmol) and 1g of $\text{ZnCo}(\text{CN})_6$ were charged to a 300 ml reactor. The contents were heated to 190°C with slow stirring. After attaining the

temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 95% conversion of urea with 45.8% selectivity to methyl carbamate, 0.8% selectivity to dimethyl carbonate and 9.7% selectivity to methyl N-methyl carbamate was observed in the reaction.

EXAMPLE 11 TO 27 FOR THE SYNTHESIS OF DMC USING CENOSPHERE

Example 11

Urea 7.5 g (120 mmol), methanol 64 g (2000 mmol) and 1 g of cenospheres were charged to a 300 ml reactor. The contents were heated to 180 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 93.6 % conversion of urea and 65.9 % selectivity to MC and ~ 1% selectivity to DMC was observed in the reaction.

Example 12

Urea 7.5 g (120 mmol), methanol 64 g (2000 mmol) and 1 g of ZnO supported on activated cenosphere. (Zn(NO₃)₂ supported on activated cenosphere (450°C) followed by calcination at 500°C) were charged to a 300 ml reactor. The contents were heated to 180 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 95.5% conversion of urea and 33.48% selectivity to MC and 3.43% selectivity to DMC was observed in the reaction.

Example 13

Urea 7.5 g (120 mmol), methanol 64 g (2000 mmol) and 1 g of activated cenosphere (activated at 450°C for 12 h) were charged to a 300 ml reactor. The contents were heated to 180 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours.

Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 96.7% conversion of urea and 20.16% selectivity to MC and 0.27% selectivity to DMC was observed in the reaction.

Example 14

Urea 7.5 g (120 mmol), methanol 64 g (2000 mmol) and 1 g of CoO supported on activated cenosphere (Co(NO₃)₂ impregnated on activated cenosphere, activated at 450°C for 12h) were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 95.2% conversion of urea and 46.8% selectivity to MC, 0.45% selectivity to DMC and 6.6% selectivity to MMC was observed in the reaction.

Example 15

Urea 7.5 g (120 mmol), methanol 64 g (2000 mmol) and 1 g of Fe₂O₃ supported on activated cenosphere (Fe(NO₃)₃ impregnated on activated cenosphere, activated at 450°C for 12h) were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 90.8% conversion of urea and 58% selectivity to MC, 0.45% selectivity to DMC and 7.8% selectivity to MMC was observed in the reaction.

Example 16

Urea 7.5 g (120 mmol), methanol 64 g (2000 mmol) and 1 g of CuO supported on activated cenosphere (Cu(NO₃)₂ impregnated on activated cenosphere, activated at 450°C for 12h) were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed

during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 87.8% conversion of urea and 53% selectivity to MC, 0.26% selectivity to DMC and 7.1% selectivity to MMC was observed in the reaction.

EXAMPLE 17

Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor. No catalyst was used. The contents were heated to 180 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and no MC conversion was observed in the reaction.

EXAMPLE 18

Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1g of cenospheres were charged to a 300 ml reactor. The contents were heated to 180 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 23% MC conversion and 14.31% selectivity to DMC was observed in the reaction.

EXAMPLE 19

Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1 g of cenospheres (activated at 450°C for 12 h) were charged to a 300 ml reactor. The contents were heated to 180 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed

by Gas Chromatography and 16% MC conversion and 34.7% selectivity to DMC was observed in the reaction.

EXAMPLE 20

Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1 g of ZnO supported on activated cenosphere. (Zn(NO₃)₂ supported on activated cenosphere (450°C) followed by calcination at 500°C) were charged to a 300 ml reactor. The contents were heated to 180 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 12% MC conversion and 20% selectivity to DMC was observed in the reaction.

EXAMPLE 21

Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1 g of CoO supported on activated cenosphere. (Co(NO₃)₂ supported on activated cenosphere (450°C) followed by calcination at 500°C for 2h and 600°C for 6h) were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 6.1% MC conversion, 5.4% selectivity to DMC, and 3.0% selectivity to MMC was observed in the reaction.

EXAMPLE 22

Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1 g of Fe₂O₃ supported on activated cenosphere. (Fe(NO₃) supported on activated cenosphere (450°C) followed by calcination at 500°C for 2h and 600°C for 6h) were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C.

Reaction mixture was analyzed by Gas Chromatography and 5.3% MC conversion, 4.7% selectivity to DMC, and 4.8% selectivity to MMC was observed in the reaction.

EXAMPLE 23

5 Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1 g of CuO supported on activated cenosphere. (Cu(NO₃)₂ supported on activated cenosphere (450°C) followed by calcination at 500°C for 2h and 600°C for 6h) were charged to a 300 ml reactor. The contents were heated to 190 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 5.8% MC conversion, 9.7% selectivity to DMC, and 3.3% selectivity to MMC was observed in the reaction.

EXAMPLE 24

15 Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and physical mixture of 1 g of Fe powder and 1g of Fe₂O₃ supported on activated cenosphere (Fe(NO₃)₃ supported on activated cenosphere (450°C) followed by calcination at 500°C for 2h and 600°C for 6h) were charged to a 300 ml reactor. The contents were heated to 190°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 3.3% MC conversion, 11.7% selectivity to DMC, and 9.2% selectivity to MMC was observed in the reaction.

EXAMPLE 25

30 Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1g of NaOH treated activated cenosphere (activated cenosphere (450°C) treated with NaOH followed by calcination at 500°C for 2h and 600°C for 6h) were charged to a 300 ml reactor. The contents were heated to 190°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the

reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 17.5% MC conversion, 13% selectivity to DMC, and 5.4% selectivity to MMC was observed in the reaction.

EXAMPLE 26

5 Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1 g of KNO₃/K₂O supported on activated cenosphere. KNO₃ supported on activated cenosphere (450°C) followed by calcination at 500°C for 2h and 600°C for 6h) were charged to a 300 ml reactor. The contents were heated to 180°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero
10 time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 21.1% MC conversion, 29%
15 selectivity to DMC, and 9.3% selectivity to MMC was observed in the reaction.

EXAMPLE 27

Methyl carbamate (MC) 7.5 g (100 mmol), methanol 64 g (2000 mmol) and 1 g of KNO₃/K₂O supported on activated cenosphere. (K(NO₃) supported on activated cenosphere (450°C) followed by calcination at 500°C) were charged to a 300 ml reactor. The contents
20 were heated to 170 °C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the
25 reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography and 26% MC conversion, 8.4% selectivity to DMC, and 1.8% selectivity to MMC was observed in the reaction.

EXAMPLE 28 TO 38 FOR THE PREPARATION OF DMC USING HYDROTALCITES AND HYDROTALCITE LIKE MATERIALS**30 Example 28**

Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor with 1g of SrAlHTlc x=3 . The contents were heated to 180°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed
35 during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at

the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 18% of conversion of MC was observed with 14% selectivity towards dimethyl carbonate (DMC).

Example 29

- 5 Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor with 1g of CaAlHTlc x=3. The contents were heated to 180°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was
10 cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 23% of conversion of MC was observed with 12% selectivity towards dimethyl carbonate (DMC).

Example 30

- 15 Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor with 1g of CaFeHTlc x=3. The contents were heated to 180°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was
20 cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 19% of conversion of MC was observed with 20% selectivity towards dimethyl carbonate (DMC).

Example 31

- 25 Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor with 1g of CoLaHTlc x=2. The contents were heated to 180°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was
30 cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 33.4% of conversion of MC was observed with 22.3% selectivity towards dimethyl carbonate (DMC).

Example 32

- 35 Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor with 1g of ZnLaHTlc (x=2). The contents were heated to 180°C with

slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 17.3% of conversion of MC was observed with 18% selectivity towards dimethyl carbonate (DMC).

Example 33

Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor with 1g of calcined LaFeHTlc ($x=3$). The contents were heated to 190°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 32.2% of conversion of MC was observed with 18.7% selectivity towards dimethyl carbonate (DMC) and 12.5% selectivity towards methyl N-methyl carbamate.

Example 34

Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor with 1g of calcined FeMnHTlc ($x=2$). The contents were heated to 190°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 42.5% of conversion of MC was observed with 12.7% selectivity towards dimethyl carbonate (DMC) and 10.6% selectivity towards methyl N-methyl carbamate.

Example 35

Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor with 1g of calcined CeMnHTlc ($x=2$). The contents were heated to 190°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia

was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 59.2% of conversion of MC was observed with 9.5% selectivity towards dimethyl carbonate (DMC) and 16.5% selectivity towards methyl N-methyl carbamate.

5 **Example 36**

Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor with 1g of calcined CeCoHTlc (x=2). The contents were heated to 190°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours.
10 Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 70.5% of conversion of MC was observed with 7.5% selectivity towards dimethyl carbonate
15 (DMC) and 22.2% selectivity towards methyl N-methyl carbamate.

Example 37

Urea 7.5 g (125 mmol) and methanol 65 g (2030 mmol) were charged to a 300 ml reactor with 1g of calcined CaAlHTlc (x=3). The contents were heated to 180°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time
20 was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 88% of
25 conversion of urea was observed with 78 % selectivity towards MC and 1.7% selectivity towards dimethyl carbonate (DMC) and 6.3% selectivity for methyl N-methyl carbamate (MMC).

Example 38

Urea 7.5 g (125 mmol) and methanol 65 g (2030 mmol) were charged to a 300 ml reactor
30 with 1g of calcined CaFeHTlc (x=3). The contents were heated to 180°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the
35 interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to 25°C. Reaction mixture was analyzed by Gas Chromatography. 95% of

conversion of urea was observed with 14 % selectivity towards MC and 5.8% selectivity towards methyl N-methyl carbamate (MMC).

Table 1. Catalyst Screening for Urea to DMC					
No.	Urea Conversion(%)	MC selectivity(%)	DMCselectivity (%)	MMC Sel (%)	Catalyst
1	88	78	1.7	6.3	CaAlHTlc(x=3 Calcined)
2*	95	14	0	5.8	CaFeHTlc (x = 3Calcined)

Reaction Conditions: Urea 7.5g (0.125M), CH₃OH 65 g(2.03M), time 8h, with NH₃ removal at every 1h, catalyst 1g, Temperature 180°C, 300ml parr reactor with condenser for NH₃ removal,* Urea 2g, CH₃OH 21.3g, without NH₃ removal, time 2h, temperature 120°C, 50cc parr reactor.

Table2. Catalyst Screening for MC to DMC			
No.	Catalyst	MC Conv (%)	DMC selectivity (%)
1	ZnFeHTlc (x=3,*Calcined)	31.42	26
2	ZnFeHTlc (x=3,\$ Calcined)	32	21
3	SrAlHTlc (x=3, Calcined)	18	14
4	CaAlHTlc (x=3, Calcined)	23	12
5	CaFeHTlc (x=3, Calcined)	19	20
6	CoLaHTlc (x=2, Calcined))	33.43	22.35
7	ZnLaHTlc (x=2, Calcined))	17.31	18
8	(0.75g) ZnFeHTlc (x=3, Calcined) + (0.25g) MK 10 (activ at 400°C)	18.5	24.56

Reaction Conditions: MC 7.5g (0.1M), CH₃OH 65 g (2.03M), temperature 180°C, time 8h, with NH₃ removal, Catalyst 1g, 300ml parr reactor with condenser for NH₃ removal, time*10h, \$5h

Table 3. Catalyst Screening for MC to DMC				
No.	Catalyst	MC Conv (%)	DMC Sel (%)	MNMC Sel (%)
1	CoLaHTlc (x=1, calcined)	35.5	19.4	9.7
2	CoLaHTlc(x=1, uncalcined)	25.4	8.1	6.2
3	LaFeHTLc(x=3, Calcined)	32.2	18.7	12.5
4	FeMnHTlc(x=2, calcined)	42.5	12.7	10.6
5	CeMnHTlc (x=2, calcined)	59.2	9.5	16.5
6	CeCoHTlc(x=2, calcined)	70.5	7.5	22.2

Reaction Conditions: MC 7.5g (0.1M), CH₃OH 65 g (2.03M), temperature 190°C, time 8h, with NH₃ removal, Catalyst 1g, 300ml parr reactor with condenser for NH₃ removal.

ADVANTAGES OF INVENTION

- i. By giving steam treatment to cenospheres the activity and selectivity of DMC can be tailored.
- ii. Acid-base properties of cenospheres can be tailored with doping of alkali, alkaline and rare earth metals to enhance the activity and selectivity.
- iii. The activity and selectivity can be enhanced by activation of cenospheres at high temperatures.
- iv. Provides environmentally benign process for the synthesis of DMC.
- v. With proper choice of divalent and trivalent metals different binary and ternary hydrotalcites can be prepared. It will be possible to tune acid base properties of hydrotalcite catalysts to improve DMC selectivity.
- vi. Di-valent and tri-valent metals used in the double metal cyanide catalysts can be varied to tailor acid-base properties of the catalyst and therefore selectivity towards DMC
- vii. The process based on catalysts disclosed here, can be improved by stripping the products ammonia and DMC from the reaction mixture

THE CLAIMS:

1. A process for the preparation of di methyl carbonate (DMC) using catalyst selected from the group consisting of double metal cyanides, cenosphere and hydrotalcites of divalent or trivalent metals catalysts and the said process comprises charging
5 urea or methyl carbamate and methanol in the range of 1:1 to 1:20, preferably 1:5 to 1:17 with the catalyst in a high pressure reactor followed by heating at temperature in the range of 100-300°C, preferably 140-200°C with stirring for period in the range of 5-10 hours with continuously removing ammonia from the
10 reactor to obtain di methyl carbonate (DMC).
2. The process as claimed in claim 1, wherein conversion percentage of urea is in the range of 80 to 99%.
3. The process as claimed in claim 1, wherein conversion of methyl carbamate is in the range of 1-99%.
- 15 4. The process as claimed in claim 1, wherein the selectivity of the process towards DMC is in the range of 1-90%.
5. The process as claimed in claim 1, wherein the said process further synthesizes MNMC from DZMC with selectivity of the process towards MNMC is in the range of 1-10%.
- 20 6. The process as claimed in claim 1, wherein the catalyst cenospheres and double metal cyanide catalyst used is optionally activated.
7. The process as claimed in claim 1, wherein the cenospheres are impregnated with metal selected from the group consisting of cobalt, iron, copper, sodium, potassium and zinc.
- 25 8. The process as claimed in claim 1, wherein divalent metals are alkaline earth metals are selected from Mg, Ca, Sr, and Ba and transition metals are selected

from Mn, Zr, Ni, Co, Cu and Zn or trivalent metals are selected from Al, Ga, Cr, Mn, Fe, Co, La, Ce, Sm and Nd.

9. The process as claimed in claim 1, wherein the catalyst used is either unsupported or supported.

10. The process as claimed in claim 1, wherein the double metal cyanide catalyst is prepared from metals selected from Ca, Fe, Zn, Co, Cu, Sn, Mg, Ni, Ce, Nd, Ba, Sr, Ce and La.

11. The process as claimed in claim 1, wherein the double metal cyanide catalyst is complexed with agents selected from polyethylene glycol, β -cyclodextrin, tween-60, tert-butanol, 1,2-dimethoxyethane, 2-methoxy ethanol, 1-methyl-2-propanol, 1,2-propanediol, tetrahydrofuran, 1,4-dioxane, hexamethylenetetramine, lactate esters with alkyl alcohols and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol).

12. The process as claimed in claim 1, wherein catalyst loading is in the range of 0.01 to 10 weight % based on urea or methyl carbamate used as a reactant.

13. The improved process as claimed in claim 1, wherein said process further synthesizes methy-N-methyl carbamate.