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(54) Title: PROCESS FOR THE SYNTHESIS OF DIMETHYLCARBONATE

(57) Abstract: The present invention discloses a process for the synthesis of dimethyl carbonate (DMC) and further methyl-N-methyl carbamate (MNMC) starting from urea or methyl carbamate using salts such as nitrate or triflate salts of rare earth elements, transition metals, alkaline earth and alkali metals as catalysts.



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PROCESS FOR THE SYNTHESIS OF DIMETHYLCARBONATE

FIELD OF THE INVENTION

5 The present invention relates to an improved process for the synthesis of dimethyl carbonate (DMC) and further methyl-N-methyl carbamate (MNMC) starting from urea or MC (methyl carbamate) using salts of rare earth elements, transition metals of group 3 to group 12 or alkaline earth and alkali metals as catalysts.

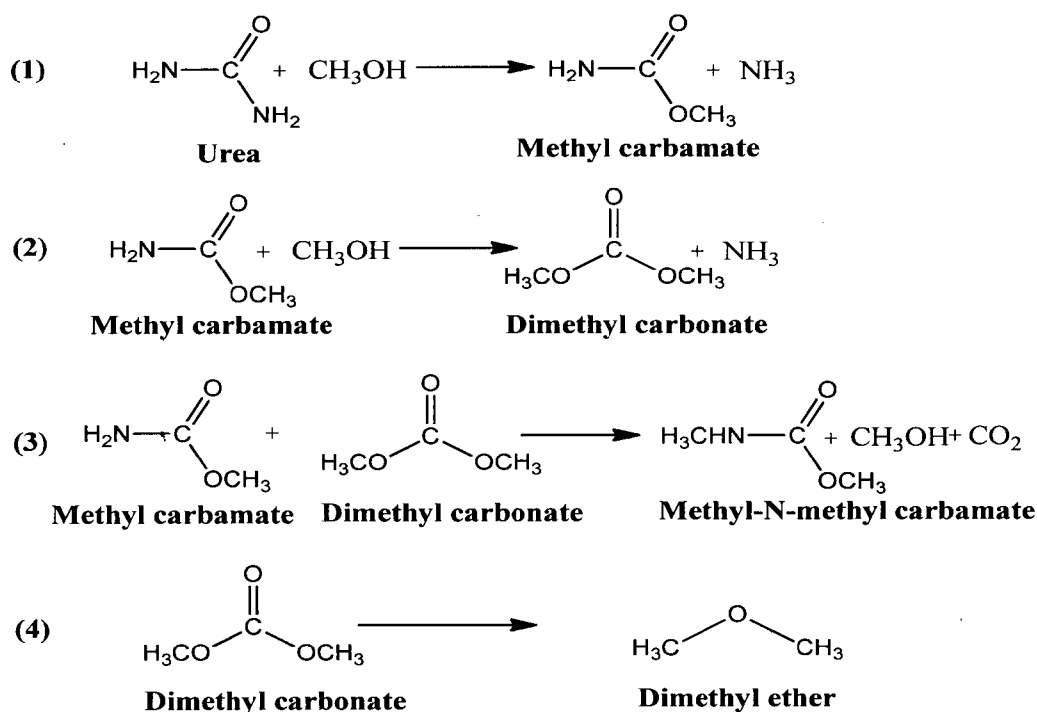
10 BACKGROUND AND PRIOR ART OF THE INVENTION

 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
15 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
20 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
25 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. Present commercial processes involve oxidative carbonylation of methanol using copper based catalyst developed by Enichem, the
30 methylnitrite carbonylation process developed by Ube Industries and transesterification of methanol with ethylene carbonate developed by Asahi Kasei Chemical, Japan. The Enichem process is hazardous in nature because of explosion risk associated with the use of CO/O₂ mixture. Similarly Ube process uses toxic NO in stoichiometric quantity and hence is environmentally unacceptable. Asahi process is environmentally benign and does not involve

any toxic chemical; however, stoichiometric production of ethylene glycol as a by-product is a major problem of this process. Significant amount of work is being carried out to develop alternative and safer route for the synthesis of DMC. Synthesis of DMC by the reaction of urea and methanol is an attractive route. This will be a GREEN Process, being based on cheap and renewable raw materials.

The reaction scheme is presented below:



There are several patents 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 overall performance of the DMC process is significantly influenced by the presence of products like ammonia and DMC in the reaction mixture because of the reversible nature of reactions. Efficient removal of by-product ammonia and product DMC formed can be used to shift the equilibrium towards right and improve the overall performance. Most of the patents and papers advocate use of reactive distillation for this purpose.

US8445713 discloses a process for preparing a catalyst for the synthesis of an organic carbonate, comprising the step of calcining a rare earth element containing hydrous salt at a calcining temperature within the range of 150°C to 450°C, wherein said rare earth element is selected from the group consisting of Preferably the rare earth element is yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, ytterbium, thorium or mixtures thereof and wherein said hydrous salt is selected from the group consisting of nitrate, sulfate, halide, phosphate, acetate and mixtures thereof.

In this case, inventors have used heterogeneous catalyst. When the inventors of the instant invention tried mixed metal oxide mentioned in US '713 as catalyst for the process of the invention by charging methyl carbamate and methanol in the range of 1 :1 to 1 : 20 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 2- 8 hours with continuously removing ammonia from the reactor to obtain dimethyl carbonate we observed 37.3 % conversion of methyl carbamate and **28.7 % selectivity to DMC** and 0.17 % selectivity to MMC was in the reaction. Refer comparative example 1.

Article titled "Synthesis of dimethyl carbonate from methyl carbamate and methanol over lanthanum compounds" by D Wang et al. published in *Fuel Processing Technology*, September 2010, Volume 91, Issue 9, Pages 1081–1086 reports **various lanthanum compounds as the catalyst for the synthesis of dimethyl carbonate (DMC) from methyl carbamate and methanol**. Among them, $\text{La}(\text{NO}_3)_3$ presented the best catalytic performance with the DMC yield of 53.7% under suitable reaction conditions. Based on the results of X-ray diffraction, Fourier transform infrared spectroscopy and element analysis, a possible reaction mechanism over lanthanum nitrate was proposed for this reaction.

Authors in Wang et al claim 63% selectivity for DMC under batch conditions, which is thermodynamically impossible. For the reversible reaction of MC to DMC the value of equilibrium constant at 180°C is about 0.01. Authors have used molar ratio of Methanol to MC of 20. Theoretically, at this mole ratio the value of equilibrium conversion is 35%. Further conversion of MC at the same mole ratio would only be possible in two ways.

- 1) Ammonia removal from reactive zone OR
- 2) DMC removal from reactive zone. DMC removal is again possible in two different modes

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- Physical removal -By means of distillation/stripping
- Chemical removal – Decomposition of DMC into byproducts

10 Since a batch reactor has been used there is no scope of physical removal of either DMC or ammonia from reaction zone. So DMC has to decompose into byproducts for this reaction to proceed beyond equilibrium conversion of 35%.

15 And Since $\text{Yield} = \text{Conversion} \times \text{selectivity}$; the value of Conversion will always be higher than Yield. In order to get yield of 53.7% yield of DMC conversion value should be atleast equal to the same value, which is thermodynamically impossible. Therefore in no circumstances possible, authors can accomplish DMC yield of 53.7% without removal of ammonia at reaction conditions mentioned.

20 WO2011013880 discloses a method for preparing dialkyl carbonate by reacting alkyl alcohol with urea or alkyl carbamate in the presence of an ionic liquid comprising a cation capable of generating a hydrogen ion (H^+), and a hydrophobic anion containing fluorine, and a catalyst comprising 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.

25 EP1629888 discloses a catalyst for the preparation of dimethyl carbonate from urea and methanol, characterized in that the catalyst has a composition on weight base of: active component: from 20 to 50 wt %, and carrier: from 80 to 50 wt %, wherein the carrier is selected from the group consisting of active carbon, α -alumina, γ -alumina, silica, and molecular sieve; and the active component is one or more selected from the group consisting
30 of oxides and chlorides of alkali metals, alkali-earth metals, and transition elements, wherein transition element is Zn, Pb, Mn, La or Ce.

Article titled “Direct synthesis of dimethyl carbonate over rare earth oxide supported catalyst” by Q Jiang published in Frontiers of Chemical Engineering in China, July 2007,

Volume 1, Issue 3, pp 300-303 reports that Solid base catalysts for the direct synthesis of dimethyl carbonate (DMC) from carbon dioxide, methanol, and propylene oxide were prepared by loading KCl and K_2CO_3 on the surface of La_2O_3 , Y_2O_3 , CeO_2 and Nd_2O_3 . The catalysts were characterized by thermogravimetric analysis (TGA) and X-ray diffraction (XRD) techniques. The catalytic activities were efficiently influenced by the preparation conditions. The optimal loading amount of K_2CO_3 is 17.6% (mass) for KCl- K_2CO_3 / Y_2O_3 and 22.2% for other catalysts. Supports affected the activity of catalyst. KCl- K_2CO_3 / Nd_2O_3 exhibited the highest activity. The activity of KCl- K_2CO_3 / Y_2O_3 increased with the increase of calcination temperature in the range of 800°C–900°C. The formation of KYO_2 , Y_3O_4Cl or YOX species probably promoted the catalysts.

Harder et al in US 4436668 titled "Preparation of Carbonates" reported the use of metal salts such as nitrates, phosphates, halides, acetates, sulfates, borates, hydroxides alcoholates, phenolates, sulfonates, oxides, oxide-hydrates, carboxylates, carbonates, thiocarbamates and dithiocarbamates as catalyst for DMC synthesis from alkyl carbamates and methanol. The preferred metal compounds are selected from the elements of groups Ia, Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb, and VIIIb of periodic table. However the examples present the activity data for metal acetates namely zinc acetate, manganese acetate, cobalt acetate for DMC synthesis under N_2 stripping conditions from urea/alkyl carbamate. Under above mentioned conditions with zinc acetate as catalyst 94% conversion of hexyl carbamate and 93% yield hexyl carbonate was realized in 58 h.

However when inventors carried out the reaction using zinc(II)acetate and yttrium(II) acetate as catalyst under reaction conditions of the process of the instant invention, very poor selectivity towards DMC was observed. With zinc(II)acetate as catalyst 44% MC conversion and 8% selectivity for DMC was observed, whereas with yttrium(II) acetate 34% MC conversion and 12.3% selectivity for DMC was obtained.

OBJECTS OF THE INVENTION

The main objective of the present invention is to provide an improved process for the preparation of dimethyl carbonate (DMC) with improved selectivity towards DMC.

Another objective of the present invention is to provide a process for the preparation of dimethyl carbonate (DMC) and further methyl-N-methyl carbamate (MNMC) starting from urea or methyl carbamate and methanol using salts of rare earth elements, transition metals of group 3 to group 12 or alkaline earth and alkali metals as catalysts.

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SUMMARY OF THE INVENTION

Accordingly, present invention provides an improved continuous process for the preparation of dimethyl carbonate (DMC) having selectivity in the range of 60 to 100% to DMC using catalyst selected from salts of rare earths, transition metals, alkaline earth and alkali metals and the said process comprising the step of:

- i. charging methyl carbamate and methanol in the ratio ranging between 1 :1 to 1 : 20 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 a period in the range of 2- 8 hours with continuously removing ammonia from the reactor to obtain dimethyl carbonate (DMC).

In an embodiment of the present invention, said rare earths, transition metals and alkaline earth and alkali metals are selected from the group consisting of La, Ce, Nd, Yb, Sm, Eu, Gd and Mg.

In another embodiment of the present invention, said salts are selected from the group consisting of methane sulphonate, triflate, nitrate and para toluene sulphonate.

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In yet another embodiment of the present invention, reactor used is selected from Parr reactors, packed bed reactors and bubble column reactors.

In yet another embodiment of the present invention, process synthesizes DMC from urea and methanol.

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In yet another embodiment of the present invention, said process further synthesizes methyl-N-methyl carbamate as by product from DMC as obtained in step (i) of claim 1 and MC.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig 1: Gas Chromatography Chart for DMC and MNMC formation with Sm (NO₃)₃ catalyst.

Fig 2: Gas Chromatography Mass Spectroscopy (GCMS) Chart for DMC and MNMC formation with Sm (NO₃)₃ catalyst.

DETAILED DESCRIPTION OF THE INVENTION

Present invention provides an Improved continuous process for the preparation of dimethyl carbonate (DMC) having greater than 60% selectivity to DMC using catalyst selected from salts of rare earths, transition metals, alkaline earth and alkali metals and the said process comprising the step of:

charging methyl carbamate and methanol in the range of 1 :1 to 1:20 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 a period in the range of 2- 8 hours with continuously removing ammonia from the reactor to obtain dimethyl carbonate (DMC).

The salts of rare earths, transition metals, alkaline earth and alkali metals are selected from methane sulphonate, triflate, nitrate and para toluene sulphonate.

The rare earths, transition metals, alkaline earth and alkali metals are selected from La, Ce, Yb, Nd, Sm, Eu, Gd and Mg.

The present invention provides catalyst system for the synthesis of DMC and further methyl-N-methyl carbamate (MNMC) starting from urea or MC comprising methane sulphonate, triflate, nitrate and para toluene sulphonate salts of rare earths, or transition metals of group 3 to group 12 or alkaline earth and alkali metals.

The present invention provides an improved process for the preparation of DMC and further methyl-N-methyl carbamate (MNMC) starting from MC.

The catalyst comprises salts of inner transition elements belonging to lanthanide and actinide series selected from, lanthanum, samarium, cerium, neodymium, gadolinium, europium, ytterbium, transition metals of group 3 to group 12 and alkaline earth and alkali metals, preferably Mg.

The catalysts are selected from Samarium (III) trifluoromethane sulfonate, Samarium (III) do-decylsulfonate, Samarium (III) methanesulfonate, Samarium (III) paratoluene sulfonate, Lanthanum (III) trifluoromethane sulfonate, Neodymium (III) trifluoromethane sulfonate, Ytterbium (III) trifluoromethane sulfonate, Europium (III) trifluoromethane sulfonate, Gadolinium (III) trifluoromethane sulfonate, Lanthanum (III) nitrate, Samarium (III) nitrate, Cerium (III) nitrate, Neodymium (III) nitrate and Magnesium (III) trifluoromethane sulfonate.

Accordingly, a 1: 1 and 1:20 ratio of MC: Methanol is reacted with catalysts as listed herein in a Parr reactor or in an autoclave to result in over 60% selectivity towards DMC. The related products formed may be DMC and MNMC. The process may optionally be conducted in a bubble column reactor or in a packed bed column reactor and the process is conducted in continuous mode.

The present invention provides an improved process for the preparation of methyl-N-methyl carbamate (MNMC) starting from urea or MC.

EXAMPLES

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

The products obtained from the process was analysed by GC, Analysis of MC and DMC were done by GC (Agilent 6890) using HP-Innowax capillary column (30m x 530µm x 1 µm) and FID detector. The method was standardized using external calibration method with known standards of MC and DMC.

Comparative Example 1

Methyl carbamate (MC) 25 g (333 mmol) and methanol 200 g (6250 mmol) with 3.4 g of CeZrO were charged to a 2000 ml reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir was fitted to reactor through constant pressure regulator which was set at 400 psi. A back pressure regulator was fitted to reactor at gas outlet valve. Back pressure regulator was set at 390 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH₃OH along with NH₃ that is formed during reaction. The reactor was then pressurized with nitrogen to 400 psi and 25 ml methanol was added to the reactor prior to heating from inlet valve. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180 °C under very slow stirring condition. After attaining the temperature the inlet valve was opened. The methanol feeding was done at the rate of 7 ml/min. The reaction was continued for 2 h. During this period methanol along with NH₃ was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH₃ was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C. Reaction mixture from bomb as well as from trap was analyzed by Gas Chromatography. From GC analysis 37.3 % conversion of methyl carbamate and 28.7 % selectivity to DMC and 0.17 % selectivity to MMC was observed in the reaction.

Example: 1

Methyl carbamate (MC) 25 g (333 mmol) and methanol 200 g (6250 mmol) with 1g of La(NO₃)₃ were charged to a 2000 ml reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 400 psi. A back pressure regulator was fitted to reactor at gas outlet valve. Back pressure regulator is set at 390 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH₃OH along with NH₃ that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 400 psi and 25 ml methanol was added to the reactor prior to heating. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180 °C under very slow stirring condition. After attaining the temperature the inlet valve was opened. The reaction was continued 2 h. During this period methanol along with NH₃ was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH₃ was collected in a trap (cooled with ice and salt mixture)

connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C. Reaction mixture from bomb as well as from trap was analyzed by Gas Chromatography. From GC analysis 29.6% conversion of methyl carbamate and 60.2% selectivity to DMC and 0.6% selectivity to MNMC was observed in the reaction.

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Example 2

The packed bed reactor comprised of a vertical stainless steel tubular reactor of 40mm I.D and 2m length. This reactor was connected to feed vessels. The column was packed with high quality randomly filled metal packings. One Vessel contains reactant solution i.e. Methyl carbamate + methanol + catalyst as reaction feed that was fed at the top of the packing. MC (187.5 g) + MeOH (1600 g) + Catalyst $\text{Sm}(\text{NO}_3)_3$ (8.67 g) solution was fed at 25°C at the rate of 3 ml/min. The temperature of the reactor was maintained at 180°C. Another vessel is fed with only MeOH at 7 ml/min rate which is heated in furnace to generate superheated methanol. Superheated methanol was fed at 195°C to the reactor from the bottom of the reactor. The function of superheated methanol is to carry the product DMC and NH_3 to the top. The reaction was carried for 9 h. During the course of reaction product DMC with methanol coming out from the top of reactor were condensed (condenser temperature 15°C) and collected in 10litre vessel. The liquid coming from the bottom of the reactor was collected in 2 litre vessel as bottom which contain unreacted MC along with catalyst and methanol. The samples were collected at 1 h interval and analysed on GC. With $\text{Sm}(\text{NO}_3)_3$ as catalyst 60.5% DMC selectivity with 32% MC conversion and 1.44 % MNMC selectivity was obtained at 180°C on packed bed reactor.

Example: 3

The Bubble column reactor comprised of vertical stainless steel bubble column reactor of 78 mm I.D. and 60 cm length. The reactions were carried out at 20-24 bar pressure. The bubble column reactor was connected to feed vessels. One Vessel contains Methyl carbamate (MC)+MeOH+Catalyst as reaction feed, which is fed to the reactor from top through the dip tube. Another vessel contains pure MeOH, which is fed to the furnace to generate superheatd methanol. Superheated methanol is fed to the reactor from the bottom and methanol vapours take ammonia and product DMC quickly out of the reaction mixture and can reduce DME formation. During the course of reaction vapors coming out from the

top of reactor were condensed (condenser temperature 15°C) and collected in overhead vessel. The liquid coming from the bottom of the reactor was collected as bottoms in a separate vessel. Reactant feed solution comprising of MC (750 g) + MeOH (1600 g) + Catalyst $\text{Sm}(\text{NO}_3)_3$ (3.5 g) was fed from top of reactor at room temperature at the rate of 3-5 ml/min was first fed to the reactor till 3.5 g catalyst was charged and desired liquid level in the reactor was attained and superheated methanol (195°C) was fed from the bottom at a flow rate of 7-10 ml/min. The temperature of the reactor was maintained at 185°C. Afterwards the feed was changed to Methanol + MC (flow rate 3 ml/min) and reaction was continued. Product DMC with methanol was collected in overhead collector and unreacted MC along with catalyst and methanol was collected at bottom. The samples were collected at 1 h interval and analysed on GC. With $\text{Sm}(\text{NO}_3)_3$ as catalyst 75% DMC selectivity with 34 % MC conversion and 4.4 % MNMC selectivity was obtained at 185°C on bubble column reactor in 6 h.

Example: 4

Methyl carbamate (MC) 228 g (3040 mmol) and methanol 147.5 g (4609 mmol) with 3g of $\text{Sm}(\text{CF}_3\text{SO}_3)_3$ were charged to a 2000 ml Parr reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 250 psi. A back pressure regulator was fitted to reactor at gas outlet valve. Back pressure regulator is set at 240 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 250 psi. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180 °C under stirring condition. After attaining the temperature the inlet valve was opened and methanol feeding was started at 7 ml/min. The reaction was continued 8h. During this period methanol along with NH_3 was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH_3 was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C. Reaction mixture from reactor as well as from trap was analyzed by Gas Chromatography. From GC analysis 58.12% conversion of methyl carbamate and 73.67% selectivity to DMC and 7.85% selectivity to MMC was observed in the reaction.

Example: 5

Methyl carbamate (MC) 228 g (3040 mmol) and methanol 147.5 g (4609 mmol) with
5 3g of $\text{Sm}(\text{CF}_3\text{SO}_3)_3$ were charged to a 2000 ml Parr reactor connected to a nitrogen reservoir
from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator
which is set at 250 psi. A back pressure regulator was fitted to reactor at gas outlet valve.
Back pressure regulator is set at 240 psi. The pressure difference of 10 psi was maintained
10 between constant pressure regulator and back pressure regulator to ensure positive flow of
nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during
reaction. The reactor was then pressurized with nitrogen atmosphere at 250 psi. The inlet
valve was closed at this point keeping outlet valve open. The contents were heated to 180 °C
under stirring condition. After attaining the temperature the inlet valve was opened and
methyl carbamate and methanol feeding was started at 7 ml/min. The reaction was continued
15 8h. During this period methanol along with NH_3 was expelled due to the set positive pressure
of nitrogen. This methanol along with dissolved NH_3 was collected in a trap (cooled with ice
and salt mixture) connected to BPR outlet. After completion of reaction the reactor was
cooled to 25°C. Reaction mixture from reactor as well as from trap was analyzed by Gas
Chromatography. From GC analysis 36.30% conversion of methyl carbamate and 72.49%
20 selectivity to DMC and 7.51% selectivity to MMC was observed in the reaction.

Example: 6

Methyl carbamate (MC) 228 g (3040 mmol) and methanol 147.5 g (4609 mmol) with
25 3g of $\text{Sm}(\text{CH}_3\text{SO}_3)_3$ were charged to a 2000 ml Parr reactor connected to a nitrogen reservoir
from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator
which is set at 250 psi. A back pressure regulator was fitted to reactor at gas outlet valve.
Back pressure regulator is set at 240 psi. The pressure difference of 10 psi was maintained
between constant pressure regulator and back pressure regulator to ensure positive flow of
30 nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during
reaction. The reactor was then pressurized with nitrogen atmosphere at 250 psi. The inlet
valve was closed at this point keeping outlet valve open. The contents were heated to 180 °C
under stirring condition. After attaining the temperature the inlet valve was opened and

methanol feeding was started at 7 ml/min. The reaction was continued 8h. During this period methanol along with NH_3 was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH_3 was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C .
5 Reaction mixture from reactor as well as from trap was analyzed by Gas Chromatography. From GC analysis 53.9% conversion of methyl carbamate and 65.7% selectivity to DMC and 7.2% selectivity to MMC was observed in the reaction.

Example: 7

10

Methyl carbamate (MC) 228 g (3040 mmol) and methanol 147.5 g (4609 mmol) with 3g of $\text{Sm}(\text{PTSA})_3$ were charged to a 2000 ml Parr reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 250 psi. A back pressure regulator was fitted to reactor at gas outlet valve.

15 Back pressure regulator is set at 240 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 250 psi. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180°C

20 under stirring condition. After attaining the temperature the inlet valve was opened and methanol feeding was started at 7 ml/min. The reaction was continued 8h. During this period methanol along with NH_3 was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH_3 was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C .

25 Reaction mixture from reactor as well as from trap was analyzed by Gas Chromatography. From GC analysis 46.5% conversion of methyl carbamate and 66% selectivity to DMC and 2.7% selectivity to MMC was observed in the reaction.

Example: 8

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Methyl carbamate (MC) 228 g (3040 mmol) and methanol 147.5 g (4609 mmol) with 3g of $\text{La}(\text{CF}_3\text{SO}_3)_3$, were charged to a 2000 ml Parr reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 250 psi. A back pressure regulator was fitted to reactor at gas outlet valve.

Back pressure regulator is set at 240 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 250 psi. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180 °C under stirring condition. After attaining the temperature the inlet valve was opened and methanol feeding was started at 7 ml/min. The reaction was continued 8h. During this period methanol along with NH_3 was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH_3 was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C. Reaction mixture from reactor as well as from trap was analyzed by Gas Chromatography. From GC analysis 61.7% conversion of methyl carbamate and 72.3% selectivity to DMC and 5.09% selectivity to MMC was observed in the reaction.

Example: 9

Methyl carbamate (MC) 228 g (3040 mmol) and methanol 147.5 g (4609 mmol) with 3g of $\text{Nd}(\text{CF}_3\text{SO}_3)_3$, were charged to a 2000 ml Parr reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 250 psi. A back pressure regulator was fitted to reactor at gas outlet valve. Back pressure regulator is set at 240 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 250 psi. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180 °C under stirring condition. After attaining the temperature the inlet valve was opened and methanol feeding was started at 7 ml/min. The reaction was continued 8h. During this period methanol along with NH_3 was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH_3 was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C. Reaction mixture from reactor as well as from trap was analyzed by Gas Chromatography. From GC analysis 58.1% conversion of methyl carbamate and 65.1% selectivity to DMC and 4.79% selectivity to MMC was observed in the reaction.

Example: 10

Methyl carbamate (MC) 228 g (3040 mmol) and methanol 147.5 g (4609 mmol) with 3g of $\text{Yb}(\text{CF}_3\text{SO}_3)_3$, were charged to a 2000 ml Parr reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 250 psi. A back pressure regulator was fitted to reactor at gas outlet valve. Back pressure regulator is set at 240 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 250 psi. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180 °C under stirring condition. After attaining the temperature the inlet valve was opened and methanol feeding was started at 7 ml/min. The reaction was continued 8h. During this period methanol along with NH_3 was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH_3 was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C. Reaction mixture from reactor as well as from trap was analyzed by Gas Chromatography. From GC analysis 48% conversion of methyl carbamate and 69.8% selectivity to DMC and 6.74% selectivity to MMC was observed in the reaction.

Example: 11

Methyl carbamate (MC) 228 g (3040 mmol) and methanol 147.5 g (4609 mmol) with 3g of $\text{Eu}(\text{CF}_3\text{SO}_3)_3$, were charged to a 2000 ml Parr reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 250 psi. A back pressure regulator was fitted to reactor at gas outlet valve. Back pressure regulator is set at 240 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 250 psi. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180 °C under stirring condition. After attaining the temperature the inlet valve was opened and methanol feeding was started at 7 ml/min. The reaction was continued 8h. During this period methanol along with NH_3 was expelled due to the set positive pressure of nitrogen. This

methanol along with dissolved NH_3 was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C room temperature. Reaction mixture from reactor as well as from trap was analyzed by Gas Chromatography. From GC analysis 58.8% conversion of methyl carbamate and 65.2% selectivity to DMC and 6.62% selectivity to MMC was observed in the reaction.

Example: 12

Methyl carbamate (MC) 228 g (3040 mmol) and methanol 147.5 g (4609 mmol) with 3g of $\text{Gd}(\text{CF}_3\text{SO}_3)_3$, were charged to a 2000 ml Parr reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 250 psi. A back pressure regulator was fitted to reactor at gas outlet valve. Back pressure regulator is set at 240 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 250 psi. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180 °C under stirring condition. After attaining the temperature the inlet valve was opened and methanol feeding was started at 7 ml/min. The reaction was continued 8h. During this period methanol along with NH_3 was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH_3 was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C room temperature. Reaction mixture from reactor as well as from trap was analyzed by Gas Chromatography. From GC analysis 59% conversion of methyl carbamate and 66.4% selectivity to DMC and 6.68% selectivity to MMC was observed in the reaction.

Example: 13

Methyl carbamate (MC) 228 g (3040 mmol) and methanol 147.5 g (4609 mmol) with 3g of $\text{Mg}(\text{CF}_3\text{SO}_3)_3$, were charged to a 2000 ml Parr reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 250 psi. A back pressure regulator was fitted to reactor at gas outlet valve. Back pressure regulator is set at 240 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of

nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 250 psi. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180°C under stirring condition. After attaining the temperature the inlet valve was opened and methanol feeding was started at 7 ml/min. The reaction was continued 8h. During this period methanol along with NH_3 was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH_3 was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C . Reaction mixture from reactor as well as from trap was analyzed by Gas Chromatography. From GC analysis 27.5% conversion of methyl carbamate and 68% selectivity to DMC and 4.07% selectivity to MMC was observed in the reaction.

Example 14

Urea 25 g (416 mmol) and methanol 220 g (6875 mmol) with 1.2g of $\text{Sm}(\text{NO}_3)_3$ were charged to a 2000 ml reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 400 psi. A back pressure regulator was fitted to reactor at gas outlet valve. Back pressure regulator is set at 390 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH_3OH along with NH_3 that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 400 psi and 25 ml methanol was added to the reactor prior to heating. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180°C under very slow stirring condition. After attaining the temperature the inlet valve was opened. The reaction was continued 2 h. During this period methanol along with NH_3 was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH_3 was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to 25°C . Reaction mixture from bomb as well as from trap was analyzed by HPLC and Gas Chromatography. From HPLC analysis 100% conversion of urea was observed. GC analysis showed 44% selectivity towards MC, 3.08 % selectivity for DMC and 1.7 % selectivity for MNMC.

Table -1: Catalyst Screening for MC to DMC (Packed Bed Reactor)							
Entry	Temp (°C)	Time (h)	Charge (g) (MC + MeOH)	MeOH (g)	MC Conv (%)	DMC Sel (%)	MNMC Sel (%)
1	180	9	1415	3331	32	60.5	1.44
Reaction Conditions: MeOH feeding rate 7ml/min, MC + MeOH feeding rate 3ml/min. Reaction Charge: MC 187.5g, MeOH 1600g, Sm(NO ₃) ₃ 8.67g							

Table -2: Catalyst Screening for MC to DMC (Bubble Column Reactor)										
Entry	MC: MeOH Ratio	Catalyst (g)	Time (h)	Charge (g) (MC + MeOH)	MeOH (g)	Feeding rate (ml/min)		MC Conv (%)	DMC Sel (%)	MNM C Sel (%)
						MC+ MeOH	MeOH			
1	1:5	3.5	6	1530	4030	3	10	34.0	75.0	4.4
Reaction Conditions: Temp., 185°C.										
Reaction Charge: MC 750g, MeOH 1600g and Sm(NO ₃) ₃ 3.5g										

Table-3: Catalyst Screening for MCto DMC (2 Litre)						
Entry	Time (h)	Temp (°C)	MC Conv (%)	DMC sel (%)	MMC sel (%)	Catalyst name
1	8	180	58.12	73.67	7.85	Sm(CF ₃ SO ₃) ₃ , Samarium (III)trifluoromethane sulfonate
2*	8	180	36.30	72.49	7.51	Sm(CF ₃ SO ₃) ₃ , Samarium (III)trifluoromethane sulfonate
4	8	180	53.9	65.7	7.2	Sm(CH ₃ SO ₃) ₃ , Samarium (III) methanesulfonate
6	8	180	46.5	66	2.7	Sm(PTSA) ₃ , Samarium (III)paratoluene sulfonate
8	8	180	61.7	72.3	5.09	La(CF ₃ SO ₃) ₃ , Lanthanum (III)trifluoromethane sulfonate
9	8	180	58.1	65.1	4.79	Nd(CF ₃ SO ₃) ₃ Neodymium (III)trifluoromethane sulfonate
10	8	180	48	69.8	6.74	Yb(CF ₃ SO ₃) ₃ Ytterbium (III)trifluoromethane sulfonate
11	8	180	58.8	65.2	6.62	Eu(CF ₃ SO ₃) ₃ Europium (III)trifluoromethane sulfonate
12	8	180	59	66.4	6.68	Gd(CF ₃ SO ₃) ₃ Gadolinium (III)trifluoromethane sulfonate
14	8	180	27.5	68	4.07	Mg(CF ₃ SO ₃) ₃ Magnesium(III)trifluoromethane sulfonate

Condition: Reaction done in 2L reactor with MC: MeOH ratio 1:1.5, MeOH feeding 7ml/min, N₂ stripping, catalyst 3g.
 *Reaction done with Mc+MeOH (1:16.5) feeding 7ml/min and N₂ Stripping

Table 4. Catalyst screening on bubble column reactor				
Catalyst	Mc conv(%)	DMC sele(%)	MMC sel(%)	MC : MeOH (g)
Sm(NO ₃) ₃ *	26	89.5	3.4	1:5
Ce(NO ₃) ₃	37.8	63.3	4.73	1:5
Sm(CH ₃ SO ₃) ₃	36.4	64	5.23	1:5
La(CF ₃ SO ₃) ₃	43.8	74.2	5.34	1:5
Sm(CF ₃ SO ₃) ₃	41.6	83.6	4.8	1:5
Reaction Conditions: Time 8h, Temperature 180°C, MeOH= 7ml/min, Catalyst 3g, Feeding rate MC+MeOH=3ml/min & MeOH= 7ml/min, MC:MeOH::1:5 * Catalyst 2g				

Example 15

- 5 The Bubble column reactor comprised of vertical stainless steel bubble column reactor of 78 mm I.D. and 60 cm length. The reactions were carried out at 15-24 bar pressure. The bubble column reactor was connected to feed vessels. One Vessel contains Methyl carbamate (MC)+MeOH as reaction feed, which is fed to the reactor from top through the dip tube. Another vessel contains pure MeOH, which is fed to the furnace to generate
- 10 superheated methanol. Superheated methanol is fed to the reactor from the bottom and methanol vapors take ammonia and product DMC quickly out of the reaction mixture and can reduce DME formation. During the course of reaction vapors coming out from the top of reactor were condensed (condenser temperature 10°C) and collected in overhead vessel. The liquid coming from the bottom of the reactor was collected as bottoms in a separate vessel.
- 15 Superheated methanol (195°C) was fed from the bottom at a flow rate of 7-10 ml/min. Reactant feed solution comprising of MC (750 g) + MeOH (1600 g) was fed from top of reactor at room temperature at the rate of 3-5 ml/min. Initially 167 g of reaction feed was added to attain desired liquid level in the reactor. This was followed by addition of 3 g of catalyst which was dissolved in 30 g of reaction feed and was added at the rate 5 ml/min from
- 20 top. The temperature of the reactor was maintained at 180°C. Afterwards the feed was changed to Methanol + MC (flow rate 3 ml/min) and reaction was continued. Product DMC with methanol was collected in overhead collector and unreacted MC along with catalyst and methanol was collected at bottom at the end of reaction. The samples were analysed on GC.

With $\text{Sm}(\text{NO}_3)_3$ as catalyst 89.5% DMC selectivity with 26 % MC conversion and 3.4 % MNMC selectivity was obtained at 180°C on bubble column reactor in 8h.

Example 16

5 The Bubble column reactor comprised of vertical stainless steel bubble column reactor of 78 mm I.D. and 60 cm length. The reactions were carried out at 15-24 bar pressure. The bubble column reactor was connected to feed vessels. One vessel contains Methyl carbamate (MC)+MeOH as reaction feed, which is fed to the reactor from top through the dip
10 tube. Another vessel contains pure MeOH, which is fed to the furnace to generate superheated methanol. Superheated methanol is fed to the reactor from the bottom and methanol vapors take ammonia and product DMC quickly out of the reaction mixture and can reduce DME formation. During the course of reaction vapors coming out from the top of reactor were condensed (condenser temperature 10°C) and collected in overhead vessel. The
15 liquid coming from the bottom of the reactor was collected as bottoms in a separate vessel. Superheated methanol (195°C) was fed from the bottom at a flow rate of 7-10 ml/min. Reactant feed solution comprising of MC (750 g) + MeOH (1600 g) was fed from top of reactor at room temperature at the rate of 3-5 ml/min. Initially 167 g of reaction feed was added to attain desired liquid level in the reactor. This was followed by addition of 3 g of
20 catalyst which was dissolved in 30 g of reaction feed and was added at the rate 5 ml/min from top. The temperature of the reactor was maintained at 180°C. Afterwards the feed was changed to Methanol + MC (flow rate 3 ml/min) and reaction was continued. Product DMC with methanol was collected in overhead collector and unreacted MC along with catalyst and methanol was collected at bottom at the end of reaction. The samples were analysed on GC.
25 With $\text{Ce}(\text{NO}_3)_3$ as catalyst 63.3% DMC selectivity with 37.8 % MC conversion and 4.73 % MNMC selectivity was obtained at 180°C on bubble column reactor in 8h.

Example 17

30 The Bubble column reactor comprised of vertical stainless steel bubble column reactor of 78 mm I.D. and 60 cm length. The reactions were carried out at 15-24 bar pressure. The bubble column reactor was connected to feed vessels. One vessel contains Methyl carbamate (MC)+MeOH as reaction feed, which is fed to the reactor from top through the dip tube. Another vessel contains pure MeOH, which is fed to the furnace to generate

superheated methanol. Superheated methanol is fed to the reactor from the bottom and methanol vapors take ammonia and product DMC quickly out of the reaction mixture and can reduce DME formation. During the course of reaction vapors coming out from the top of reactor were condensed (condenser temperature 10°C) and collected in overhead vessel. The liquid coming from the bottom of the reactor was collected as bottoms in a separate vessel. Superheated methanol (195°C) was fed from the bottom at a flow rate of 7-10 ml/min. Reactant feed solution comprising of MC (750 g) + MeOH (1600 g) was fed from top of reactor at room temperature at the rate of 3-5 ml/min. Initially 167 g of reaction feed was added to attain desired liquid level in the reactor. This was followed by addition of 3 g of catalyst which was dissolved in 30 g of reaction feed and was added at the rate 5 ml/min from top. The temperature of the reactor was maintained at 180°C. Afterwards the feed was changed to Methanol + MC (flow rate 3 ml/min) and reaction was continued. Product DMC with methanol was collected in overhead collector and unreacted MC along with catalyst and methanol was collected at bottom at the end of reaction. The samples were analysed on GC. With $\text{Sm}(\text{CF}_3\text{SO}_3)_3$ as catalyst 83.6% DMC selectivity with 41.6 % MC conversion and 4.8 % MNMC selectivity was obtained at 180°C on bubble column reactor in 8h.

Example 18

The Bubble column reactor comprised of vertical stainless steel bubble column reactor of 78 mm I.D. and 60 cm length. The reactions were carried out at 15-24 bar pressure. The bubble column reactor was connected to feed vessels. One vessel contains Methyl carbamate (MC)+MeOH as reaction feed, which is fed to the reactor from top through the dip tube. Another vessel contains pure MeOH, which is fed to the furnace to generate superheated methanol. Superheated methanol is fed to the reactor from the bottom and methanol vapors take ammonia and product DMC quickly out of the reaction mixture and can reduce DME formation. During the course of reaction vapors coming out from the top of reactor were condensed (condenser temperature 10°C) and collected in overhead vessel. The liquid coming from the bottom of the reactor was collected as bottoms in a separate vessel. Superheated methanol (195°C) was fed from the bottom at a flow rate of 7-10 ml/min. Reactant feed solution comprising of MC (750 g) + MeOH (1600 g) was fed from top of reactor at room temperature at the rate of 3-5 ml/min. Initially 167 g of reaction feed was added to attain desired liquid level in the reactor. This was followed by addition of 3 g of catalyst which was dissolved in 30 g of reaction feed and was added at the rate 5 ml/min from

top. The temperature of the reactor was maintained at 180°C. Afterwards the feed was changed to Methanol + MC (flow rate 3 ml/min) and reaction was continued. Product DMC with methanol was collected in overhead collector and unreacted MC along with catalyst and methanol was collected at bottom at the end of reaction. The samples were analysed on GC.

5 With La (CF₃SO₃)₃ as catalyst 74.2% DMC selectivity with 43.8 % MC conversion and 5.34 % MNMC selectivity was obtained at 180°C on bubble column reactor in 8h.

Example 19

10 The Bubble column reactor comprised of vertical stainless steel bubble column reactor of 78 mm I.D. and 60 cm length. The reactions were carried out at 15-24 bar pressure. The bubble column reactor was connected to feed vessels. One vessel contains Methyl carbamate (MC)+MeOH as reaction feed, which is fed to the reactor from top through the dip tube. Another vessel contains pure MeOH, which is fed to the furnace to generate
15 superheated methanol. Superheated methanol is fed to the reactor from the bottom and methanol vapors take ammonia and product DMC quickly out of the reaction mixture and can reduce DME formation. During the course of reaction vapors coming out from the top of reactor were condensed (condenser temperature 10°C) and collected in overhead vessel. The liquid coming from the bottom of the reactor was collected as bottoms in a separate vessel.
20 Superheated methanol (195°C) was fed from the bottom at a flow rate of 7-10 ml/min. Reactant feed solution comprising of MC (750 g) + MeOH (1600 g) was fed from top of reactor at room temperature at the rate of 3-5 ml/min. Initially 167 g of reaction feed was added to attain desired liquid level in the reactor. This was followed by addition of 3 g of catalyst which was dissolved in 30 g of reaction feed and was added at the rate 5 ml/min from
25 top. The temperature of the reactor was maintained at 180°C. Afterwards the feed was changed to Methanol + MC (flow rate 3 ml/min) and reaction was continued. Product DMC with methanol was collected in overhead collector and unreacted MC along with catalyst and methanol was collected at bottom at the end of reaction. The samples were analysed on GC. With Sm(CH₃SO₃)₃ as catalyst 64% DMC selectivity with 36.4 % MC conversion and 5.23
30 % MNMC selectivity was obtained at 180°C on bubble column reactor in 8h.

ADVANTAGES OF THE INVENTION

- Novel catalyst system
- High selectivity towards DMC

CLAIMS

1. An improved continuous process for the preparation of dimethyl carbonate (DMC) having selectivity in the range of 60 to 100% to DMC using catalyst selected from salts of rare earths, transition metals, alkaline earth and alkali metals and the said process comprising the step of:
 - i. charging methyl carbamate and methanol in the ratio ranging between 1 :1 to 1 : 20 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 a period in the range of 2- 8 hours with continuously removing ammonia from the reactor to obtain dimethyl carbonate (DMC).
2. The process according to claim 1, wherein said rare earths, transition metals and alkaline earth and alkali metals are selected from the group consisting of La, Ce, Nd, Yb, Sm, Eu, Gd and Mg.
3. The process according to claim 1, wherein said salts are selected from the group consisting of methane sulphonate, triflate, nitrate and para toluene sulphonate.
4. The process according to claim 1, wherein reactor used is selected from Parr reactors, packed bed reactors and bubble column reactors.
5. The process according to claim 1, said process synthesizes DMC from urea and methanol.
6. The process according to claim 1, wherein said process further synthesizes methyl-N-methyl carbamate as by product from DMC as obtained in step (i) of claim 1 and MC.

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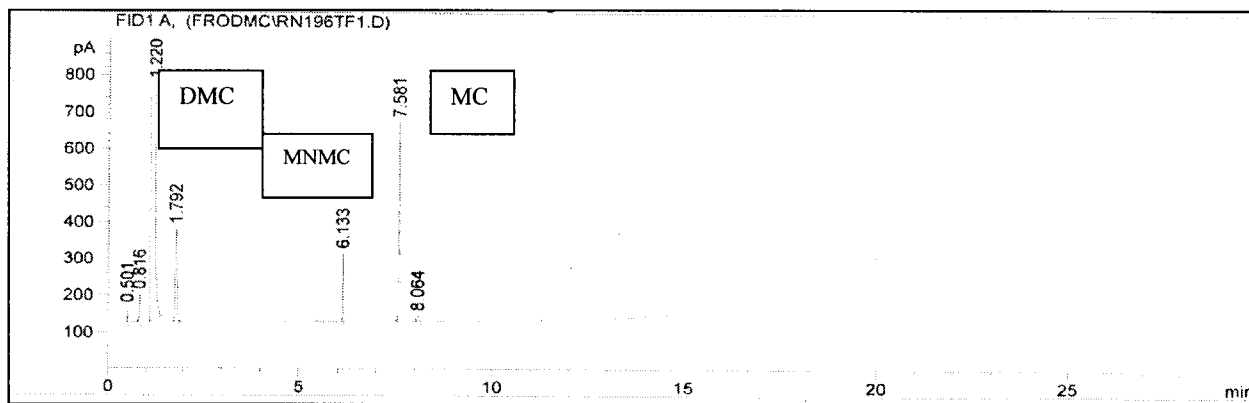


Fig 1

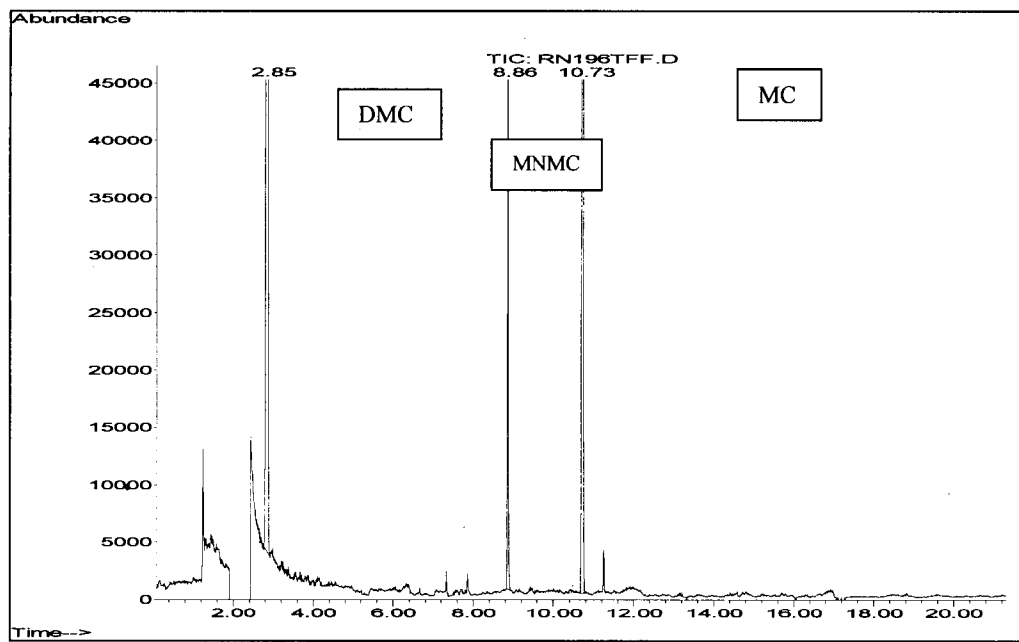


Fig 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2015/000109

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C68/00 C07C69/96 C07C269/00 C07C271/12 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 534 649 A (CHO TSURAHIDE [JP] ET AL) 9 July 1996 (1996-07-09) abstract; claims 1,3 column 3; examples 2-5; table 1 -----	1,6
X	D. WANG ET AL.: "Synthesis of Dimethyl Carbonate from Methyl Carbamate and Methanol Using a Fixed-Bed Reactor", CHEMICAL ENGINEERING & TECHNOLOGY, vol. 35, no. 12, 6 December 2012 (2012-12-06), pages 2183-2188, XP55202221, ISSN: 0930-7516, DOI: 10.1002/ceat.201200217 abstract; figures 1,7 page 2185, column 1, paragraph 1 page 2186, paragraph 3.2 - page 2187 ----- -/--	1,4,6
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 14 July 2015		Date of mailing of the international search report 28/07/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Kiernan, Andrea

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2015/000109

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 4 436 668 A (HARDER WOLFGANG [DE] ET AL) 13 March 1984 (1984-03-13) cited in the application abstract; claims 1,3,5-7 pages 7-8; examples 23-25 -----	1,6
Y	WO 2009/052996 A1 (BAYER MATERIALSCIENCE AG) 30 April 2009 (2009-04-30) cited in the application abstract; claims 17-20 examples 1-10,14,15 page 8 -----	1-6
Y	ZHAO, W. ET AL.: "Zinc oxide as the precursor of homogenous catalyst for synthesis of dialkyl carbonate from urea and alcohols", CATALYSIS COMMUNICATIONS, vol. 10, no. 5, 25 January 2009 (2009-01-25), pages 655-658, XP025770511, ISSN: 1566-7367, DOI: 10.1016/J.CATCOM.2008.11.018 [retrieved on 2008-11-24] page 656; example 6; table 1 -----	1-6
Y	ZHAO, W. ET AL.: "Reaction Mechanism and Kinetics of Dimethyl Carbonate Synthesis from Methyl Carbamate and Methanol", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 51, no. 51, 26 November 2012 (2012-11-26), pages 16580-16589, XP55202195, ISSN: 0888-5885, DOI: 10.1021/ie302245n abstract page 16581, paragraph 3.1.; figure 1 ----- -/--	1-6

INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2015/000109

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	----- DATABASE ZCAPLUS, [Online] 2010, WANG, D. ET AL.: "Synthesis of dimethyl carbonate from methyl carbamate and methanol catalyzed by cerium compounds", XP002728301, retrieved from ZCAPLUS Database accession no. 2010-328838 abstract	1-6
Y	----- WANG DENG FANG ET AL: "Synthesis of dimethyl carbonate from methyl carbamate and methanol catalyzed by ionic liquids", SHIYOU HUAGONG - PETROCHEMICAL TECHNOLOGY, vol. 39, no. 4, 2010, pages 387-390, XP008175250, ISSN: 1000-8144 abstract page 388, paragraph 2.1; table 1	1-6
Y	----- ARESTA, M. ET AL.: "NEW CATALYSTS FOR THE CONVERSION OF UREA INTO CARBAMATES AND CARBONATES WITH C1 AND C2 ALCOHOLS", STUDIES IN SURFACE SCIENCE AND CATALYSIS, vol. 153, 2004, pages 213-220, XP008056377, ISSN: 0167-2991, DOI: 10.1016/S0167-2991(04)80251-9 pages 217-218, paragraph 2.6.-2.8.; tables 1,2 ----- -/--	1-6

INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2015/000109

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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