

DIMETHYL CARBONATE PRODUCTION FOR FUEL ADDITIVES.

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Abstract

We have taken note of the transesterification reaction as a highly safe process of dimethyl carbonate (DMC) production for fuel additives. The reaction proceeds under the low corrosiveness and in the relatively mild condition. We have aimed to use an inorganic solid catalyst for this process. The inorganic solid catalyst is thermally stable and can be used in the large-scale fixed bed reactors without a catalyst separation unit.

Through the transesterification of ethylene carbonate(EC) with methanol, DMC and ethylene glycol (EG) are co-generated as the products⁽¹⁾.



EG is one of the bulk chemicals produced in the large scale plant comparable to one for the fuel additives. The market balance is important in the co-production process. On the assumption that the amount of the co-production meets the market balance, the co-production of DMC and EG is commercially viable. If we can control the amount of the EG co-production in this process, it makes the process more flexible in the commercial production. Accordingly we have proposed a conceptual process scheme to control the amount of the EG co-production.

In this symposium, the inorganic solid catalyst system applying to the transesterification process and the conceptual process scheme how to control the amount of co-product will be discussed.

1.Introduction

Dimethyl carbonate (DMC) is very attractive as for use as an oxygenate for the fuel additives. Many routes of the DMC synthesis have been proposed. Among those routes, the DMC production process for the chemical raw material has been commercialized. The process for the fuel additives should be easy to scale up in the capacity to satisfy the large demand. Moreover, it is also required to be safe in the operation and to be stable in the supply.

2.Selection of DMC synthesis route

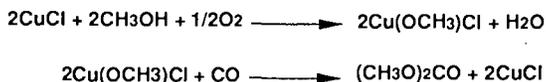
2-1 Probable routes of DMC synthesis

DMC is produced several ten thousands ton per year in the world as chemical raw material used in the carbonylating and methylating agent, etc. DMC had been formerly produced from phosgene. The proposed synthesis methods including commercialized routes as non-phosgene DMC production are classified generally into the following 4 routes. Fig.1 shows the relation of raw materials and intermediates of those routes. All routes start from methanol. There is the other route to produce DMC using nitrous acid ethers⁽²⁾ except in Fig.1. This route has been in commercial for the chemical raw material use. Though the nitrous acid ethers are less toxic than phosgene, they are still considered as toxic materials. Accordingly, we put the process using nitrous acid ethers out of our research scope. The investigation results of the routes shown in Fig.1 are the following.

2-2 Oxidative carbonylation route

Oxidative carbonylation processes in both the liquid phase and the vapor phase have been developed. The liquid phase oxidative carbonylation is the oxidation of carbon monoxide with oxygen in methanol in the presence of copper chloride⁽³⁾. The catalyst is used in a slurry mixture. Now, DMC for the chemical use is being produced in this oxidative carbonylation process. In the vapor phase oxidative carbonylation, palladium chloride-copper chloride⁽⁴⁾, cupric chloride on activated carbon⁽⁵⁾, etc. is proposed as the catalyst. All of these oxidative carbonylation processes including technologies under development inevitably need the presence of both oxygen gas and chloride.

In these situation, Chiyoda Corporation has tried to investigate halogen-free solid catalysts to improve the oxidative carbonylation process in the view point of less corrosiveness and the separability of the catalyst. We have succeeded to find the zeolite fixed the cation of copper as this kind catalyst which is particularly effective as the catalyst of the following reactions.



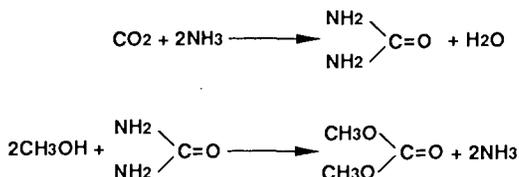
2-3 Esterification route

The route from carbon dioxide and methanol into DMC through the dehydration is the simplest one. We have tried it challengingly. Since this reaction is very disadvantageous in the equilibrium, the reaction could not be successfully proceeded.



2-4 Route through urea

In this route, firstly urea is synthesized from carbon dioxide and ammonia. Subsequently, the urea reacts with methanol into DMC.



Though methyl carbamate is easily generated as mono-changed intermediate in the second reaction step, the intermediate can not be transformed into DMC.

2-5 Transesterification route (glycol co-production route)

As shown in Fig. 1, ethylene carbonate (EC) is used as the raw material instead of the direct reaction of carbon dioxide in the transesterification route. The EC is commercially produced from carbon dioxide and ethylene oxide. Subsequently, DMC is obtained from the EC through the transesterification with methanol. Ethylene glycol (EG) is converted from ethylene oxide as a main

co-product in this route. EG produced conventionally through the hydration of ethylene oxide is one of the bulk chemicals quantitatively comparable to fuel additives. In this transesterification route, the dried EG can be produced.

We have studied zeolite catalysts applying to the co-production of DMC and EG through the transesterification reaction. Zeolite catalysts have the excellent properties of resistance to heat and organic solvents and can be used in the large fixed bed reactors without a catalyst separation unit. We have found that some of zeolites have catalytic activity to the transesterification reaction. These results were presented at 207th ACS National Meeting. The catalytic activity depends on the Al_2O_3/SiO_2 ratio which represents the quantity of active sites. Since zeolite A has a maximum value of the Al_2O_3/SiO_2 ratio at 0.5 in the various type zeolites, the zeolite shows the highest activity. The cation species in the zeolite have an influence to the catalytic activity, the order of the activity is; $3A (KA) > 4A (NaA) > 5A (CaA)$.

2-6 Selection of the DMC synthesis route

Transesterification reaction is mild with small exotherm, and is carried out in the liquid phase without any toxic or corrosive chemicals. Therefore, it is essentially safe. Moreover, these features will be the merit in scaling up, because the large production will be able to perform with a low fixed capital.

In consideration of the above, we have selected the transesterification route as the most suitable one to large scale production of DMC for fuel additives and proceeded the further research in focus on this route.

3. The conceptual process of DMC production for fuel additives

3-1 The co-production of DMC and EG through the transesterification reaction

Fig. 2 shows the conceptual process scheme of DMC production through the transesterification route. Fig. 3 shows the concrete concept of the process scheme. The scheme consists of 9 units (blocks), ie. transesterification reactor, DMC-McOH / EG-EC separation unit, MeOH separation unit, EC hydration reactor, etc. In the scheme, EG is co-produced quantitatively comparable to DMC.

3-2 The concept to control the EG co-production

If we can produce the only DMC or control the amount of the EG co-production in the selected route, it will make the process more flexible in the commercial production. This concept means that the large DMC production is possible freely from the demand of EG. Fig. 4 shows the process scheme of the advanced concept. In this scheme, the co-produced EG is required to re-convert into the started EC. Accordingly, we have investigated the reaction to re-convert EG into EC.

In the first, we have conducted a test of the transesterification of EG and DMC, which is a reverse reaction of DMC and EG co-production. EC and methanol were generated with intermediate in stoichiometric proportions. It has been confirmed this transesterification is a reversible reaction. Therefore, we have considered EG would be able to re-convert into EC on the preferable catalyst. From the investigation of various reaction with the catalyst, we have confirmed that EC is generated from EG using urea instead of DMC.



3-3 The conceptual process of DMC production controlled the EG co-production

It is considered the combination of the EC regeneration reaction and urea synthesis makes the DMC production process controlled the EG co-production possible. Fig.5 shows the conceptual process scheme. In the scheme, urea is the intermediates synthesized from carbon dioxide and ammonia. Since the process of urea synthesis from carbon dioxide and ammonia had been established commercially, we can avail the process into the our proposed process complex without basic research. Fig.6 shows the total reaction scheme on which this conceptual process are based. In this reaction scheme, the DMC is synthesized from carbon dioxide and methanol through the dehydration reaction by the several steps.

4.Conclusion

we have selected the transesterification route as the most suitable one to large scale production of DMC for fuel additives. Transesterification reaction is mild with small exotherm, and is carried out in the liquid phase without any toxic or corrosive chemicals. Therefore, it is essentially safe. Moreover, these features will be the merit in scaling up. Zeolites can be used as the catalysts of this reaction. The zeolite catalysts have the excellent properties of resistance to heat and organic solvents and can be used in the fixed bed reactors without a catalyst separation unit.

EG is co-produced with DMC in the transesterification route. EG is one of the bulk chemicals quantitatively comparable to the fuel additives. On the assumption that the amount of the co-production meets the market balance, the co-production of DMC and EG is commercially viable.

As the option for this process, we have investigated the concept for the only DMC production or the control of the amount of the EG co-production. This concept means that the large DMC production is possible freely from the demand of EG. We have proposed the conceptual process scheme of the DMC production controlled the amount of the EG co-production. The conceptual process is consist of the urea synthesis and the re-conversion of EG into EC. In this conceptual process scheme, the DMC is synthesized from carbon dioxide and methanol through the dehydration reaction by the several steps. We have confirmed that EC is generated from EG using urea with the catalyst. However, the improvement of the catalyst and the investigation of the reaction conditions for the EC regeneration are required to rise the DMC yield in the total process.

5.References

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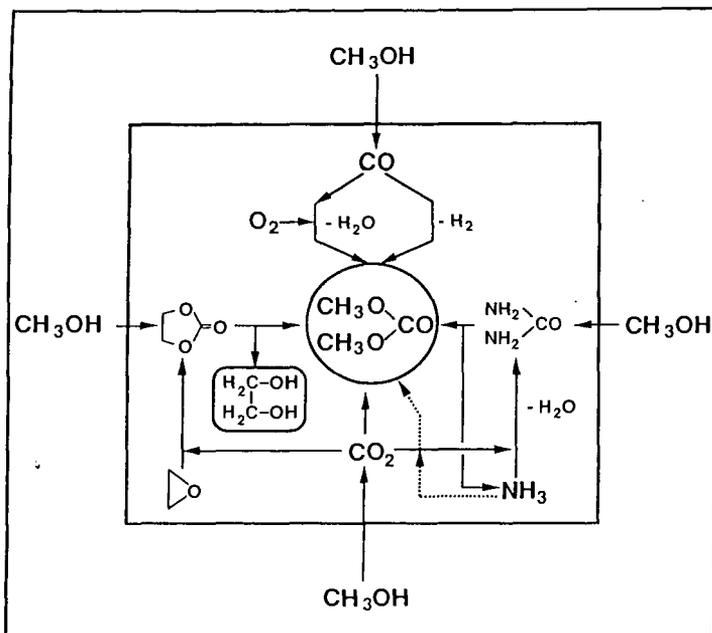


Fig.1 Routes of DMC synthesis without Cl_2CO



DMC:Dimethyl carbonate EC: Ethylene carbonate EG: Ethylene glycol

Fig.2 The conceptual process scheme of the DMC and EG co-production through the transesterification route

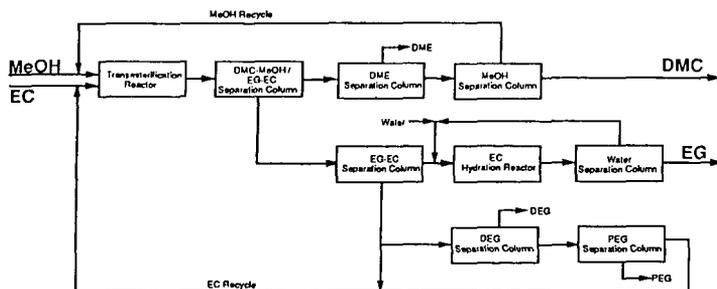
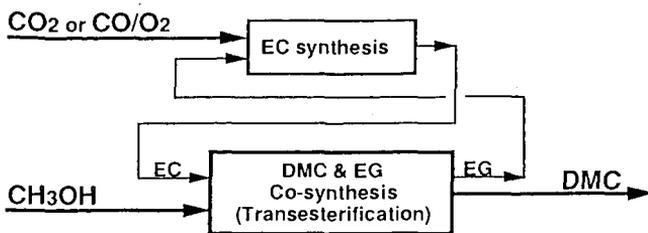
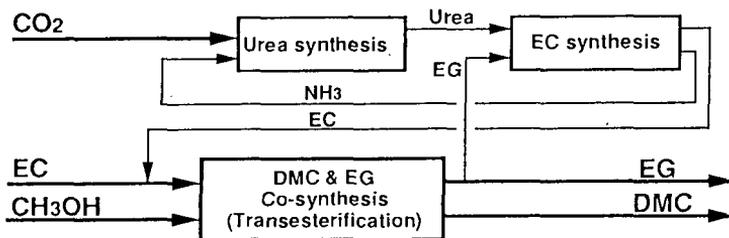


Fig.3 The concrete concept of the DMC and EG co-production process through the transesterification route



DMC:Dimethyl carbonate EC: Ethylene carbonate EG: Ethylene glycol

Fig.4 The conceptual process scheme of the DMC production without the EG co-production through the transesterification route



DMC:Dimethyl carbonate EC: Ethylene carbonate EG: Ethylene glycol

Fig.5 The conceptual process scheme to control the EG co-production in the DMC production through the transesterification route

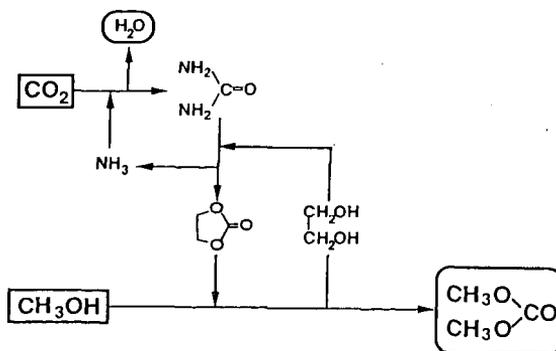


Fig.6 The reaction scheme of DMC synthesis from CH_3OH and CO_2