Innovative process for carbonates from CO_2

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Abstract:

We have successfully developed an innovative process for producing diphenyl carbonate (DPC) using CO_2 as raw material. DPC is an excellent carbonyl source replacing poisonous phosgene in the production of polycarbonates and isocyanates. Our process uses organometallic compound to directly activate CO_2 and produce dialkyl carbonate (DRC). In the next step, DRC is reacted with phenol and in the overall reaction, DPC is produced from phenol and CO_2. This novel process solves many problems such as the use of poisonous raw materials and therefore it is considered to be “GSC process” due to the safety of raw materials, high selectivity, and high efficiency of energy.

Keywords: Diphenyl carbonate, Dialkyl carbonate, CO_2, GSC Process.

1. Introduction

In the production of polycarbonates and isocyanates, phosgene and carbon monoxide are still widely used as raw material. The reactivity of these compounds is very high, but there is demerit because of the very high toxicity of compounds. Moreover, both processes are involving chlorine compound and as the result, there are several technical problems such as corrosion in the reactor and contamination of chlorine compound in the product. Carbon dioxide has low reactivity and the reaction is limited by low equilibrium constant but there are merits such as very low toxicity and low price of raw material. Toxicity is the original property of the compound itself therefore the only way to solve this problem is to take the safety (precaution) measures. But, instead of taking safety (precaution) measures, it is important to use safe raw materials and design a real safe process.

Synthesis of carbonic acid ester by using hydroxyl compound (alcohol) and CO_2 is the ideal process because water is the only by-product. However, low reactivity and equilibrium limitation are problems. We found that these problems can be solved by using appropriate catalyst and process development.

2. Theoretical

In the synthesis of carbonic ester using carbon dioxide as starting compound, the reactivity is very low and the reaction is limited by the extremely small equilibrium constant (Fig.1). As the result, the yield of DRC from this method is not worth considering. In order to solve the equilibrium limitation, it is necessary to remove water from reaction system effectively.

There is a method that introduces dehydrants into the reaction system and the dehydrants are proved to shift the reaction to the right side and improve the yield of DRC. But the separation and recycle of deactivated dehydrants are difficult problems and these make the production cost expensive and also make the commercialization impossible. The development of water removal process is the key to solve equilibrium limitation.

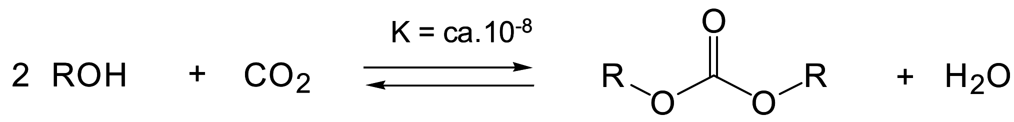

Figure 1. The equilibrium limitation in the synthesis of carbonic ester using CO_2.

3. Results and discussion

The extremely small equilibrium constant that limit the reaction is solved by developing new reaction system. We found that the equilibrium limitation can be solved by using metal alkoxide as intermediate and separating the reaction into several steps. The new reaction system consist 3 steps (Fig.2). In the first step, the carbonate production, the metal alkoxide complex is reacted with gaseous CO_2 and the produced CO_2

adduct complex is then thermally decomposed to DRC and metal alkoxide residue. In the second step, the DRC is separated from the reaction mixture and the metal alkoxide residue is then introduced to the next step. In the last step in which the metal alkoxide is recycled, the metal alkoxide residue is reacted with alcohol and the water produced is collected by distillation and as the result the residue is reactivated to the metal alkoxide. By repeating these 3 steps, DRC is produced by using alcohol and carbon dioxide as reactants and metal alkoxide as intermediate. Thus, the equilibrium limitation can be solved by designing new reaction system and moreover each step is independent therefore each reaction can be extended stoichiometrically at its optimal condition.

The produced DRC is then reacted with phenol to produce DPC (Fig.3). The reaction system consist 2 steps. In the first step, the transesterification is conducted by reacting DRC with phenol to produce alkyl phenyl carbonate. In the second step, the disproportion of alkyl phenyl carbonate is conducted to produce DPC. We found that the waste and energy consumption are reduced due to the high selectivity and the non-azeotropic of compounds. In the overall reaction, DPC is produced from phenol and CO_2.

We are verifying the newly developed process to produce DPC via DRC by conducting continuous operation in our validation plant. We will continue to verify the economy and energy efficiency of the new process, and work toward its further optimization as a highly energy-efficient process that utilizes CO_2.

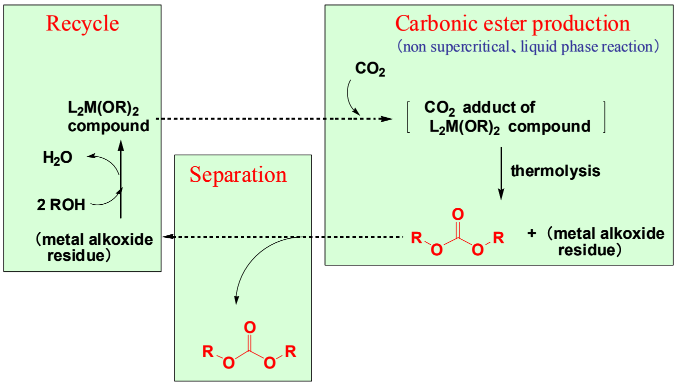

Figure 2. The dialkyl carbonate production process.

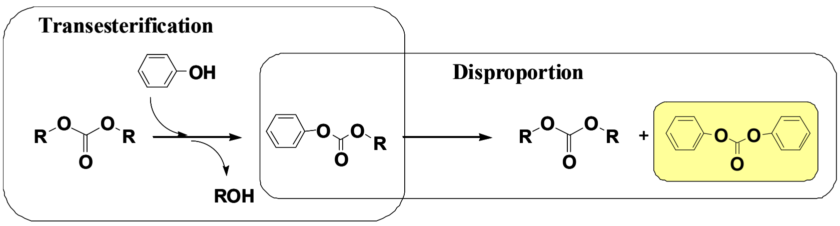

Figure 3. The diphenyl carbonate production process.

4. Conclusions

We developed the environment friendly process that uses CO_2 and hydroxyl compound to produce carbonic ester. The process has characteristics such as low energy consumption and small amount of waste. This novel process solves many problems such as the use of poisonous raw materials and therefore it is considered to be "GSC process" due to the safety of raw materials, high selectivity, and high efficiency of energy.

References

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