

K/MgO

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Continuous Production of Dimethyl Carbonate Using K/MgO Fixed-Bed Catalyst

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Introduction

Recently, dimethyl carbonate (DMC, b.p. = 90°C, $M_w = 90$) has been known as a useful compound having versatile uses. In many aspects, DMC can be variously applied as a solvent in carbonylation and methylation as well as a gasoline octane enhancer. Due to the negligible toxicity of DMC, it is promising as a substitute for phosgene, dimethyl sulfate and methyl chloride. Mostly, DMC has been synthesized by reaction of methanol with phosgene. However, recent research has focused on establishing environmentally benign non-phosgene method for the production of DMC.

So far, a number of DMC synthetic processes have been suggested and some processes have already been commercialized. For example, EniChem and Ube have developed the oxidative carbonylation of methanol and the carbonylation of methylnitrite processes, respectively. Besides, vapor phase oxidative carbonylation of methanol, transesterification, urea alcoholysis, esterification of methanol and electrochemical method are being approached for DMC synthetic process development. Especially, the process for the cosynthesis of DMC and ethylene glycol through the transesterification of ethylene carbonate (EC) with methanol has been developed by Texaco Chemical Co. and carried out.

In transesterification route, while method using homogeneous catalysts has the advantage of high catalytic activity and reaction rate, there is the drawback that separation and recovery of the catalyst from reaction liquid accompany essentially. Since heterogeneous catalysts can be easily separated from the reaction liquid, the methods using them are free from the problems involved in the homogeneous catalysts. Thus, methods using inorganic solid catalysts as heterogeneous catalysts have been proposed. In this work, DMC was continuously synthesized from EC and methanol using K/MgO fixed-bed catalyst.

Experimental

MgO (Source: Daejung Chem. Co.) pellet was prepared to be used as a support. MgO pellet was shaped with its powder through a series of procedure. The produced MgO pellets were impregnated with K_2CO_3 aqueous solution for 5 h, dried in an oven at 100°C overnight and calcined in an electric furnace at 300-550°C for 5 h. All the experiments were carried out in a vertical tube reactor (Length: 1/2 in., Volume: 25 mL, SUS316) as a continuous liquid phase system. The reactor was mounted in a jacket furnace controllable to $\pm 1.0^\circ C$. As a preliminary step, K/MgO powder catalyst was employed for measuring its activity in the flow system. And it was considered as a standard to be compared with that of K/MgO pellet catalyst. Reaction conditions and procedures are as follows.

K/MgO catalyst pellets or powder was charged in the tube reactor and glass wool was plugged at the top and bottom of reactor to ensure the catalyst powder or pellets remain in the reactor. Mixture of methanol and EC (MeOH/EC molar ratio = 4.0) as a feed was introduced into the reactor by HPLC pump (Gilson Medical Electronics, Model 305) at a flow rate range of 2.5 - 25 mL/h. The reaction temperature range was changed from 50 to 125°C and the reaction pressure was maintained to be

constant by BPR (Back Pressure Regulator). Reaction pressure was generally held for reactants not to be vaporized. Fig. 1 shows the schematic diagram of experimental apparatus.

The output product was analyzed using a gas chromatograph (Gow-Mac 550P) equipped with a TCD detector and a Carbowax column (1/8 in. \times 2m, Chrom W-HP, 80/100).

Results and Discussion

K/MgO pellets or powder has been used in a continuous catalytic system for DMC synthesis. Its activity and fundamental reactive characteristics were intensively investigated.

Fig. 2 shows that effect of reaction temperature on DMC yield. Reaction temperature was changed in the range of 100 – 150°C. As shown in Fig. 1, DMC yield of around 50% was obtained in the reaction conditions of 150°C and LHSV=0.1. DMC yield increased along with reaction temperature and resident time. However, an unknown by-product began to appear at 150°C and LHSV= 0.5 or 0.1. So, the reaction condition of 125°C and LHSV= 0.1 was more desirable to DMC synthesis in continuous system. DMC yield is too low to be over 15% at 100°C and LHSV = 1.0. Fig. 3 shows the effect of K content in catalyst on DMC yield. The content of K in K/MgO powder are 0.69, 5.03 and 9.77 wt.%. K contents in K/MgO powder catalysts were analyzed by AAS (Atomic Absorption Spectrophotometer). As content of K in K/MgO increased, DMC yield increased. In K content of 9.77 wt.%, DMC yield increased up to around 51% without the formation of any by-product formation. Generally, DMC yield was observed to be greatly affected by K content in K/MgO. BET surface areas of three different catalysts were also investigated each another. BET surface areas were measured as 7.49, 4.67 and 3.97 m²/g in K contents of 0.69, 5.03 and 9.77 wt.%, respectively. As a standard experimental result for comparison, surface area of the used MgO powder was 58.42 m²/g before any treatment and was 10.56 m²/g after calcination at 550°C. BET surface area was decreased along with an increment of the impregnated K content. As shown in Fig. 3, however, DMC yield increasing was not affected by the loss of surface area. In spite of that, DMC yield was improved slightly. That means that this liquid phase reaction system do not require greatly the high surface area of employed heterogeneous catalyst. In relatively low surface area, it is strongly believed to be possible that catalytic reaction takes place well by the proper arrangement of optimal K component in the catalyst.

Fig. 4 shows long-term activity test for K/MgO pellet catalyst in the DMC synthesis. In the condition of LHSV= 0.1, it takes 10 h for reactant to pass reactor. So, some reaction time was required to be steady-state. After steady-state, DMC yield of around 52-53% was maintained to be constant. As shown in Fig. 4, K/MgO pellet could hold constantly its catalytic activity more than around 1440 h (= 2 months) for DMC synthesis.

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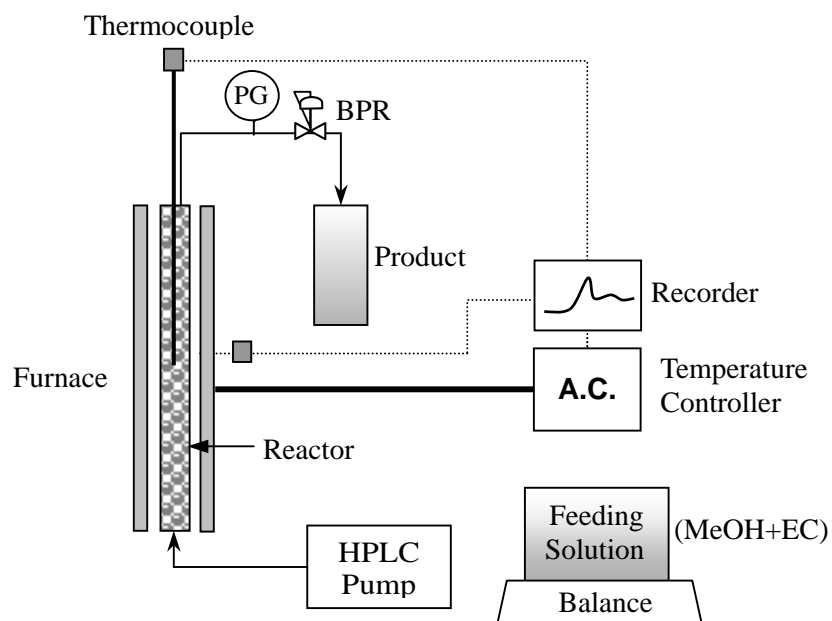


Fig. 1. Schematic diagram of experimental apparatus.

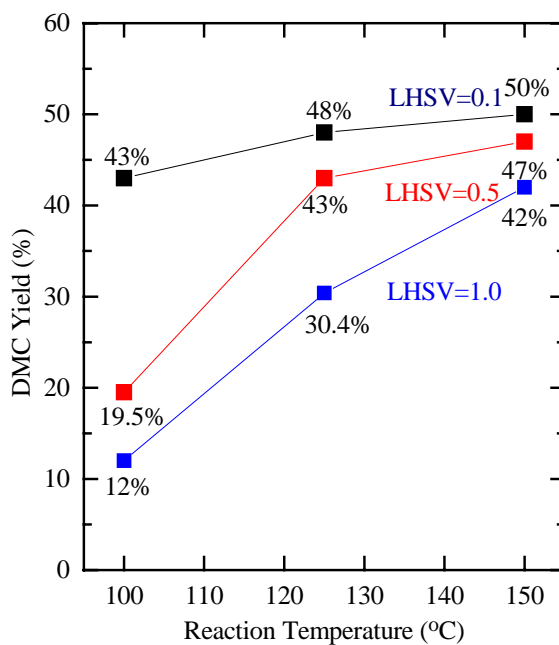


Fig. 2. Effect of reaction temperature on DMC Yield (LHSV: 0.1-1.0 h⁻¹, Reaction flow rate: 2.5-25 ml/h, MeOH/EC molar ratio: 4.0, Catalyst: K/MgO-550°C calcined powder, K content: 5 wt.%)

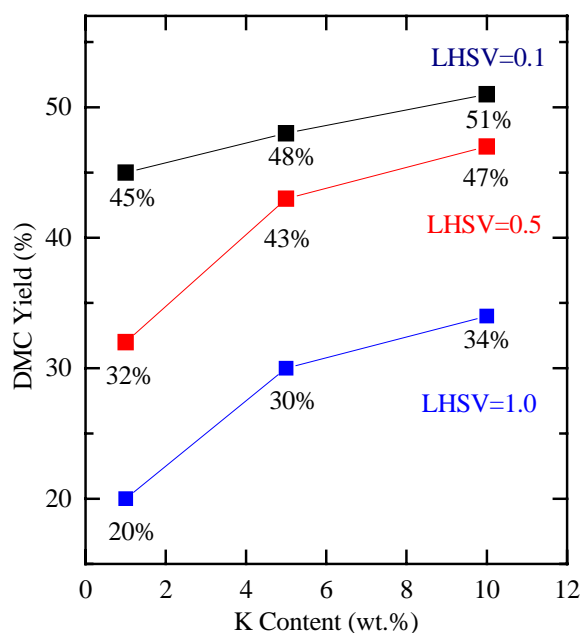


Fig. 3. Effect of K content in catalyst on DMC Yield (LHSV: 0.1-1.0 h⁻¹, Reaction flow rate: 2.5-25 ml/h, MeOH/EC molar ratio: 4.0, Catalyst: K/MgO-550°C calcined powder, Reaction temperature: 125°C)

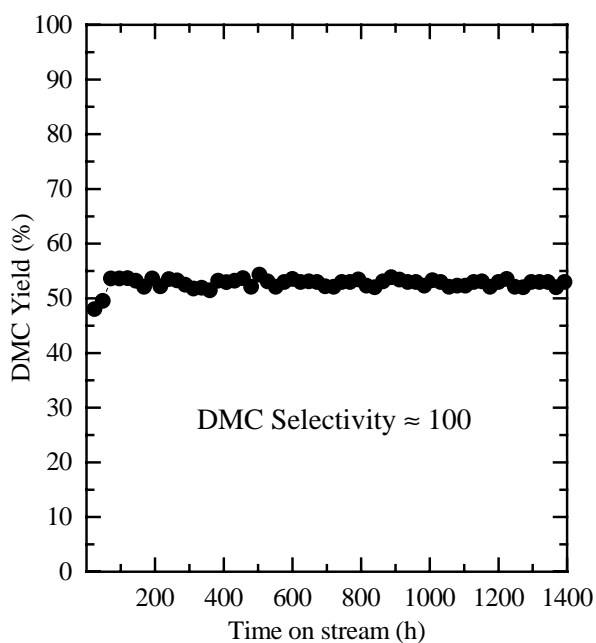


Fig. 4. Long-term activity test for K/MgO pellet catalyst in the DMC synthesis (LHSV: 0.1 h⁻¹, Reaction flow rate: 2.5 ml/h, MeOH/EC molar ratio: 4.0, Catalyst: K/MgO-300°C calcined pellet, Reaction temperature: 125°C, Total run time: around 1400 h ≈ 2 months)