CeO_2-catalyzed ring-opening polymerization of trimethylene carbonate

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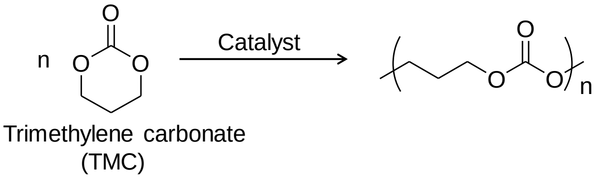
Abstract: Ring-opening polymerization of cyclic carbonates is a promising method for the synthesis of polycarbonates with high purity, and it can be regarded as one of substitution methods for conventional phosgene process. Herein, we demonstrate that cerium oxide (CeO_2) calcined at 1273 K is an effective heterogeneous catalyst for the synthesis of polytrimethylene carbonate by ring-opening polymerization of trimethylene carbonate. High yield of polytrimethylene carbonate yield (99%) was achieved, and the M_n value reached 17,000.

Keywords: Ring-opening polymerization, Cerium Oxide, Aliphatic polycarbonate.

1. Introduction

Aliphatic polycarbonates with high biocompatibility, facile biodegradation and low toxicity are promising chemicals in food and medical applications. Polycarbonates have been industrially produced from diol and phosgene as a carbonyl source. However, phosgene is highly toxic, and the process produces a large amount of salts by neutralization. Therefore, phosgene-free methods have been intensively investigated, such as condensation of diols and organic carbonates as a carbonyl source[1], copolymerization of cyclic ethers and CO_2 as a carbonyl source[2], ring-opening polymerization of a cyclic carbonate[3], and direct copolymerization of CO_2 and diols[4]. Among these methods, the ring-opening polymerization is a promising method due to the purity of produced polycarbonates.

Homogeneous catalysts such as metal complexes[5] and Brønsted acids[6] have been used, but there are some problems such as difficulty in separation and reusability of the catalyst. Heterogeneous catalysts are preferable in terms of the reusability and separation, however, there is only one example of immobilized enzyme on silica[7]. In this study, we investigated effective catalysts for the ring-opening polymerization of trimethylene carbonate (TMC), and found that CeO_2 calcined at 1273 K showed high activity for the reaction, and achieved M_n=17,000.



Scheme 1 Ring-opening polymerization of trimethylene carbonate (TMC).

2. Experimental

Various metal oxides (Y_2O_3, CeO_2, Al_2O_3, La_2O_3, ZrO_2, ZnO, MgO, TiO_2) were calcined at 873 K in air for 3 h. Y_2O_3, CeO_2 and Al_2O_3 were calcined at temperatures from 873 K to 1473 K in air for 3 h. All the reactions were carried out in an autoclave reactor with inner volume of 190 mL. Reaction conditions were as follows: catalyst, 0.17 g; TMC, 10 mmol (1.02 g); Ar, 1 MPa; 333 K; 250 rpm. After the reaction time, the product was collected from the autoclave reactor with 15 mL THF. The substrate and products were analyzed by GC, HPLC, MALDI-TOF mass, SEC and ^{1}H-NMR. Characterization of catalysts were analyzed by XRD, BET method, NH_3, CO_2-TPD and NMR. Tetramer and longer polymers were assigned to polymer in this study.

3. Results and discussion

Activity tests were performed using various metal oxides calcined at 873 K (Figure 1). Without catalyst, low conversion and low M_n (the number average molecular weight) were obtained. Y_2O_3, CeO_2 and Al_2O_3 exhibited high conversion, high selectivity to polymer (>95%) and moderate M_n value (>4000). On the other hand, La_2O_3, ZrO_2, ZnO, MgO and TiO_2 showed lower conversion than Y_2O_3, CeO_2 and Al_2O_3. Therefore, Y_2O_3, CeO_2 and Al_2O_3 are selected as candidates of effective catalysts for the reaction.

Next, we investigated the effect of calcination temperature on the catalytic performance with Y_2O_3, CeO_2 and Al_2O_3 catalysts, and compared the activity per specific surface area. Y_2O_3, CeO_2 and Al_2O_3 calcined at 873-1473 K were used for the reaction (Figure 2). In the case of Y_2O_3 and Al_2O_3, the activity was not drastically changed by increasing the calcination temperature, while M_n with Y_2O_3 calcined at 1073 K was quite higher than Y_2O_3 catalysts with the other calcination temperatures. On the other hand, the activity of CeO_2 increased with increasing the calcination temperature. It should be noted that the activity of CeO_2 calcined at 1273 K was 10 times higher than that of CeO_2 calcined at 873 K. Moreover, a high M_n value using CeO_2 calcined at 1273 K was obtained in comparison with CeO_2 catalysts calcined at the other calcination temperatures. Therefore, CeO_2 calcined at 1273 K was the most effective for ring-opening polymerization of TMC.

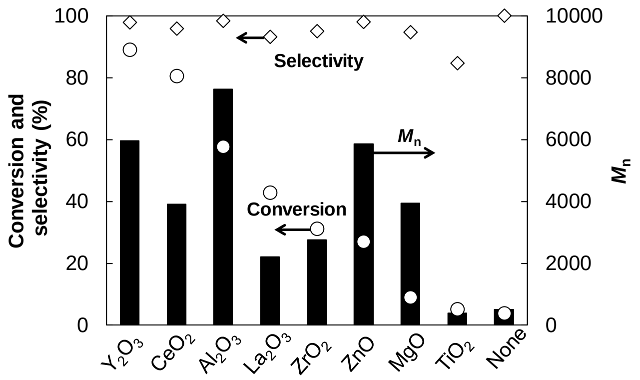


Figure 1. Catalyst screening for ring-opening polymerization of TMC. Reaction conditions: TMC 10 mmol, catalyst 1 mmol (based on metal), Ar 1.1 MPa, 333 K, 24 h.

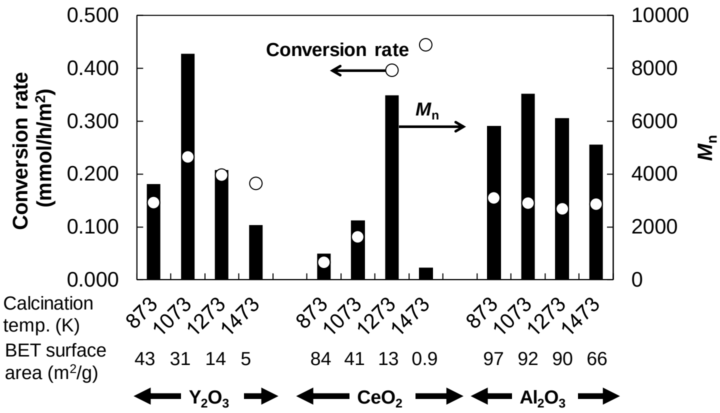


Figure 2. Effect of calcination temperature of Y_2O_3, CeO_2, Al_2O_3 catalysts on ring-opening polymerization of TMC. Conversion rate is based on surface area.
Reaction conditions: TMC 10 mmol, catalyst 1 mmol (based on metal), Ar 1.1 MPa, 333 K, 8 h.

The time-course of the ring-opening polymerization was investigated using CeO_2 catalyst calcined at 1273 K. Both conversion and M_n increased with the reaction time. The reaction proceeded to reach 99% yield of polytrimethylene carbonate in 24 h, and the highest M_n of 17,000 was achieved. MALDI-TOF mass spectrum of the produced polycarbonate showed the peaks with the regular interval (102 m/z), which corresponds to the molecular weight of the single unit of polytrimethylene carbonate. These results indicate that the polymer was formed from ring-opening polymerization of TMC.

4. Conclusions

CeO_2 catalyst calcined at 1273 K showed high activity for the synthesis of polytrimethylene carbonate by ring-opening polymerization of trimethylene carbonate (TMC). Catalytic activity per surface area of CeO_2 calcined at 1273 K was 10 times higher than that of CeO_2 calcined at 873 K. High polytrimethylene carbonate yield of 99% was achieved, and the M_n value of 17,000 was obtained. MALDI-TOF mass spectroscopy revealed that the produced polycarbonate was formed from ring-opening polymerization of TMC.

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