

CO₂ Fixation in Polymers

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Introduction

The utilization of CO₂ formed during burning fossil fuels as chemical feedstock places new opportunities to avoid the release of CO₂ into the atmosphere. CO₂ can be reacted directly with highly reactive chemicals to form products with lower exergy than the sum of the starting materials. A typical example is the copolymerization between epoxides and CO₂ to form aliphatic polycarbonates. Alternatively, CO₂ conversion can be achieved by removal of a by-product from the reaction equilibrium or by coupling with an exergonic reaction. An example is the synthesis of dimethylcarbonate by direct methanolysis of CO₂ whereby the byproduct water is removed to shift the equilibrium to the products.

Experimental

For the methanolysis of urea, a mixture of methanol (30 ml), urea (2 g) and catalyst (0.5 g) was heated in a 70 ml autoclave. After 4 hours, the product mixture was analyzed by gas chromatography.

Direct CO₂ fixation in co-polymers

Carbon dioxide can be utilized in the synthesis of aliphatic polycarbonates by copolymerization of CO₂ and epoxides. Suitable catalysts are, e.g., ZnEt₂ activated by trace amounts of water (1), zinc oxide (2), salen complexes (3), double metal cyanides of iron and zinc (4), zinc glutarate (5) or rare earth – zinc catalyst mixtures (6). While mostly ethylene and propylene oxide were used, other epoxides, such as limonene oxide are also suitable (7). Recently a copolymer synthesized by this route came into industrial production in China (8). There is a possibility that the substitution of purely aliphatic polymers by polycarbonates will reduce alkene consumption and CO₂ emission into the atmosphere by millions of tons, since CO₂ is fixed in 50 wt-% in the CO₂-ethylene oxide copolymer (1).

Synthesis of dimethylcarbonate

Alkyl carbonates are a valuable feedstock for chemical synthesis and, e.g., can be converted to polycarbonates. The direct synthesis of dialkylcarbonates from alcohols and carbon dioxide is equilibrium limited to conversions below 10%, but can be accomplished starting from orthoester using organotin compounds like Bu₂Sn(OMe)₂ / Bu₄PI as molecular catalysts (9). Likewise, urea can be reacted with methanol to dimethylcarbonate. Among various oxides, zirconia (Fig. 1) and tin oxide provided the highest catalytic activity. An approach for the direct synthesis of dimethylcarbonate from methanol and CO₂ is to remove the by-product water using a dehydrating agent (10).

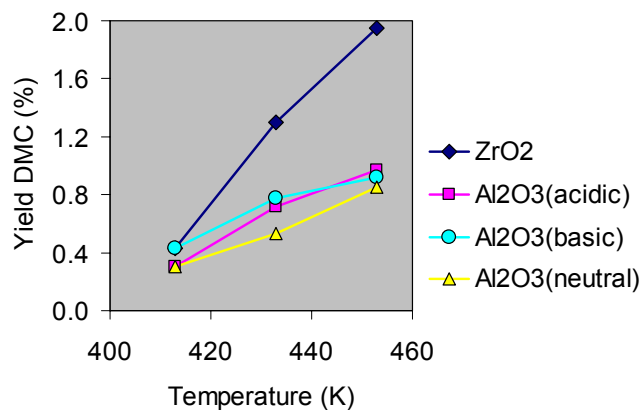


Figure 1. Comparison of catalyst activity in the methanolysis of urea.

Conclusions

As new technologies are emerging, the direct utilization of CO₂ as chemical reagent appears to be a possible strategy to avoid carbon dioxide emissions into the atmosphere. Scientific and political interests meet leading to strongly increased awareness in this field.

References

- (1) Koinuma, H. *React. Funct. Polymers*, **2007**, *67*, 1129.
- (2) Huang, s.; Liu, S.; Li, J.; Zhao, N.; Wie, W.; Sun, Y. *Catal. Lett.* **2007**, *118*, 290–294.
- (3) Darensbourg, D. J.; Mackiewicz, R. M.; Phelps, A. L. and Billodeaux, D. R. *Acc. Chem. Res.* **2004**, *37*, 836-844.
- (4) Darensbourg, D. J.; Adams, M. J.; Yarbrough, J. C. and Phelps, A. L. *Inorg. Chem.* **2003**, *42*, 7809-7818.
- (5) Ree, M.; Hwang, Y.; Kim, J.-S.; Kim, H.; Kim, G.; Kim, H. *Cat. Today* **2006**, *115*, 134–145.
- (6) Quan, Z.; Wang, X.; Zhao, X.; Wang, F. *Polymer* **2003**, *44*, 5605.
- (7) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B. and Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 11404-11405.
- (8) Kawaguchi, T.; Nakano, M.; Juni, K.; Inoue, S.; Yoshida, Y. *Chem. Pharm. Bull.* **1983**, *31*, 1400–1403.
- (9) T. Sakakura, Saito, Y.; Okano, M.; Choi, J. C. and Sako., T.; *J. Org. Chem.*, **1998**, *63*, 7095.
- (10) Choi, J. C.; He, L. N.; Yasuda H. and Sakakura, T. *Green Chemistry*, **2002**, *4*, 230–234.