From syngas to electrolyte solutions for Li-ion batteries: Design of green chemical routes

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Abstract: This paper reports a green chemical route for the synthesis of alkyl carbonate from synthesis gas ($CO+H_2$) by alcoholysis of urea followed by the transesterification between methanol/ethanol and cyclic carbonate, using solid base catalysts.

Keywords: Green Chemistry, Cyclic carbonate, Lithium ion battery.

1. Introduction

As one of the main constituents of lithium ion battery system, the electrolyte solution, composed of alkyl carbonates including ethylene carbonate, dimethyl, diethyl, and ethyl-methyl carbonates (EC, DMC, DEC, EMC, respectively), and $LiPF_6$, functioned as an important bridge to connect the anode and cathode of the battery. The alkyl carbonates were chosen due to their acceptable anodic stability for the 4 V cathodes used in Li-ion batteries, as well as lithiated graphite, together with other properties, such as high polarity (i.e., good conductivity of their solutions), a reasonable temperature range between freezing and boiling points, sufficiently low toxicity, and acceptable safety features. Therefore, the synthesis processes of these alkyl carbonates and the catalysts had received extensive attention by the researchers all over the world.

So far, various routes, such as the phosgenation of methanol, the oxidative carbonylation of methanol, alcoholysis of urea or the transesterification between methanol and cyclic carbonate, and so on had been explored to synthesize alkyl carbonate. The phosgenation of methanol is a traditional route for the synthesis of these carbonates, however, this process takes use of phosgene, an intense toxic substance as the main reactant, and also co-produces hydrochloric acid, which results in a serious erosion of the equipments and environment demolishment. The route of oxidative carbonylation of methanol with carbon monoxide and oxygen may be a better route for the synthesis of DMC, owing to its low cost of raw materials. However, it is dangerous and potentially explosive due to the utilizations of carbon monoxide and oxygen mixture as starting materials.

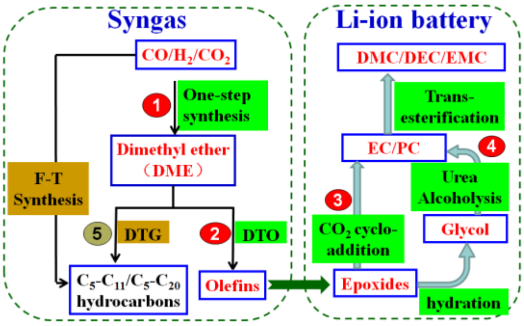

Figure 1. Schematic diagram for the synthesis of Li-ion battery electrolyte solution from synthesis gas.

In this report, a green chemical route (**Fig. 1**) for the synthesis of alkyl carbonate were designed and synthesized from synthesis gas ($CO+H_2$) by alcoholysis of urea followed by the transesterification between methanol/ethanol and cyclic carbonate, using solid base catalysts. This two-step green chemical route showed many advantages such as low price of feedstock, mild conditions, and the yield of alkyl carbonate is more skillful than that of others process. However, this process is limited by the chemical equilibrium, therefore the exploration of high efficient catalyst is the key factor to solve the problem.

2. Experimental

Two different types of catalysts were designed and prepared. The first one used in the alcoholysis of urea from glycol is an acid-base bifunctional catalyst, composed by Zn and Al composite oxides. The catalyst used in the transesterification is the strong base catalyst prepared by the impregnation process. The strong base, KOH or KF, was used as active ingredient, while H-Beta, 4A, SAPO-18, ZSM-5 and NaX were used as supports.

The performance of the catalyst for the DTO reaction was performed in an integral fixed-bed reactor (φ 30 mm × 550 mm) at atmospheric pressure. The experimental processes of urea alcoholysis and transesterification were carried out in a 50 ml stainless steel autoclave equipped with a temperature controlling system and a magnetic stirrer.

3. Results and discussion

3.1 Dimethyl ether (DME) to olefins over AEI/CHA Intergrowth Zeolites

The conversion of methanol (directly or indirectly via DME) to olefins (MTO or DTO) over SAPO catalysts has sparked continuing industrial and academic interest in the past decades, due to their high selectivity towards light olefins (about 80% in total). Moreover, the methanol and DME can be easily produced via synthesis gas (syngas, CO/H_2) from other abundant nonpetroleum feedstocks such as natural gas, coal and biomass. In the present time, SAPO-18 (AEI) and SAPO-34 (CHA) are the two preferred shape-selective catalysts for the MTO or DTO reaction. The catalytic lifetime can be significantly improved by the application of SAPO-18 due to its lower density and weaker strength of the Brønsted acid sites. However, the high-cost in preparation and difficulty in separation and recovery limit the practical application of SAPO-18 zeolites. Rapid coke formation and frequent regeneration does take place on SAPO-34 owing to its bigger crystalline size and higher surface acid density, although the facile synthesis, separation and recovery processes. We have discovered that AEI/CHA intergrowth materials are highly efficient for the DTO reaction, while SAPO-18/34 intergrowth zeolites with higher AEI/CHA ratio and smaller particle size under less template usage and milder conditions, made the DTO process more economical and environment-friendly. **Fig. 2** shows the products distribution of the prepared samples. It can be seen that the selectivity of the generated products changes with the variation of phase composition in the catalysts. The ethylene selectivity declines, while the propylene and butylene selectivities enhance with the increasing of AEI/CHA ratio in the catalysts, indicating that CHA phase is favorable for the formation of ethylene, and AEI phase favors propylene and butylene.

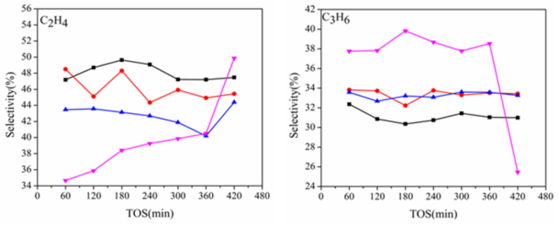

Figure 2. Products distribution over the catalysts synthesized at various template compositions.
1.6DEA (■), 1.4DEA+0.2DIEA (●), 0.2DEA+0.4DIEA (▲), 1.6DIEA (▼).

3.2 Synthesis of ethylene carbonate by Zn-Al composite oxide catalysts

The synthesis of ethylene carbonate (EC) from urea and glycol was carried out over Zn–Al composite oxide catalysts derived from hydrotalcites (HTs). The catalytic results showed that the hydrotalcites calcined at 450 ℃ with Zn : Al = 3 : 1 exhibited superior catalytic activity, and the highest EC yield was 92.8%. Figure 3 shows the CO_2-TPD of the catalysts with the aim of establishing a relationship between performance and alkalinity. It indicates that the four groups of Zn/Al hydrotalcite catalysts showed different amount of alkalinity. With the decrease of Zn:Al ratio, the peak position of moderately strong alkaline sites gradually moves to low temperature, indicating that the alkalinity of four kinds of Zn/Al hydrotalcite catalysts decreases gradually. The catalytic results indicated that Zn_3Al with appropriate accessible active medium basic sites were favorable for obtaining much superior catalytic activity.

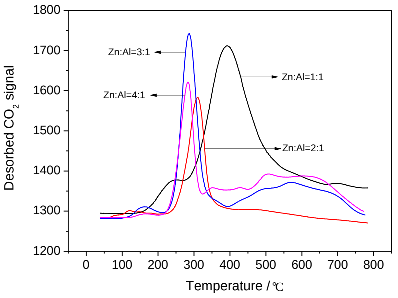

Figure 3 The CO_2-TPD curves of hydrotalcite with different Zn/Al molar ratio.

4. Conclusions

The green chemical route for the synthesis of electrolytes for Li-ion battery can be realized by designing appropriate catalyst.

References (Omit)