Clean synthesis of ethyl methyl carbonate using Mg-Al mixed oxide as catalyst

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Abstract. A series of Mg-Al mixed oxides were prepared by the calcination of Mg-Al layered double hydroxides with various Mg/Al molar ratios (2-6) at different temperature (400-700°C), and used as catalyst for the transesterification synthesis of ethyl methyl carbonate (EMC). The results showed that Mg/Al molar ratio and roasting temperature had remarkable effect on the activity of Mg-Al mixed oxides. Among investigated catalysts, MgAlO-3-600 showed the highest activity. And 51.6% EMC yield can be obtained at 100°C within 1.5 h. In addition, MgAlO-3-600 could be reused at least 4 times without obviously loss of its activity for the EMC synthesis.

1. Introduction

As a kind of important asymmetric carbonate, ethyl methyl carbonate (EMC) is an important organic carbonate electrolyte, which can improve the discharge capacity and energy density of lithium-ion batteries. Traditionally, EMC is prepared by the reaction of chloroformate and CH₃CH₂OH using stoichiometric strong base as catalyst. However, this method is not an environmentally process due to the highly toxic methyl of chloroformate. Another route to synthesis EMC is the transesterification of dimethyl carbonate (DMC) with ethanol. In the reaction process, however, three binary azeotropes (DMC-methanol, DMC-ethyl alcohol, and EMC-ethyl alcohol) are formed, causing serious separation difficulties. In addition, EMC can also be synthesized by transesterification of diethyl carbonate (DEC) with DMC. The main advantage of this method is that the separation process can be avoided because all reaction mixtures (DEC, DMC and EMC) can be used as solvents in non-aqueous electrolytes [1-4]. Zhou et al. [2] reported that 50.1% yield of EMC was obtained by using MOF-5 as catalyst at 100°C within 3 h. However, MOF-5 was sensitive to air and moisture. Recently, ZIF-8 showed excellent stability, high catalytic activity and good reusability for this reaction reported by our group [3]. Nowadays, it is still important to develop cheap, available, efficient and stable heterogeneous catalysts for the industrial synthesis of EMC.

Hydrotalcite type layered double hydroxides (LDH) are natural or synthetic materials with the general formula of [M₁⁺ₐM₂⁺ⁿ(OH)₂][Xᵇ⁻]ₙ·aH₂O. LDH has been widely used in the fields of heat stabilizer, flame retardant, adsorbent, medicine and catalyst. LDH can be converted into metal mixed oxides after calcination, and its specific surface area and surface alkali content are increased significantly, which makes it show high alkali catalytic activity and well reusability.

Herein, Mg-Al mixed oxides, prepared by the calcination of Mg-Al layered double hydroxides (LDH) precursors, are developed as cheap, available, highly efficient and reusability heterogeneous catalyst for the transesterification synthesis of EMC. We found that the composition, structure and
catalytic activity of Mg-Al mixed oxides can be tailored by simple exchange of Mg/Al molar ratio and/or roasting temperature.

2. Experimental

2.1. Catalyst preparation and characterization

Mg-Al LDH precursors were prepared by the co-precipitation method. In a typical procedure, aqueous solutions containing various Mg/Al molar ratios (Mg/Al=2, 3, 4, 5 and 6) of Mg(NO$_3$)$_2$ and Al(NO$_3$)$_3$ were added to a 0.5 L flask containing 0.1 L deionized water. The pH of the reaction solution was maintained at 10.0 using a solution mixture of Na$_2$CO$_3$ and NaOH. Both solutions were added dropwise at 40°C for 2 h under vigorous stirring. The slurry was aged at 60°C for 20 h. And the resulting precipitate was filtered and washed with deionized water until neutral. The solid was dried at 120°C for 8 h to yield Mg-Al LDH precursors, which were further calcined at 600°C for 5 h in air to obtain the Mg-Al mixed oxides. The prepared samples were denominated as MgAlO-X-T (X: Mg/Al molar ratio, T: calcination temperature).

The powder of X-ray diffraction patterns (XRD) were tested on X-ray diffractometer (XPERT PRO) using a Cu K radiation source (λ=1.54056Å), operating at 40 kV and 45 mA. The diffraction pattern was recorded in the scanning range of 5−90° with the scanning rate of 5°/min and 0.03° step size.

2.2. Catalytic reactions

The synthetic process of EMC was as follows: DMC (9.00 g, 100 mmol) and DEC (11.80 g, 100 mmol) were added into a 50 ml flask equipped with reflux condenser and magnetic stirring. The temperature was raised to 100°C with stirring. Then, 0.208 g catalyst was added into the reaction system. The reaction time was 1 h under the condition of continuous stirring. After the reaction, the reactant was cooled to room temperature and the catalyst was separated by filtration. The filtrate was analyzed quantitatively by GC (SP-6890, China) and qualitatively by GC-MS (HP 6890/5973). After filtration and separation, the catalyst was washed with ethanol and dried, and then used for the next run of EMC synthesis.

3. Results and discussion

3.1. Characterization of catalyst

The powder XRD patterns of Mg-Al LDH precursors were showed in Figure 1. All patterns contained the characteristic peaks corresponding to a well-defined hydrotalcite-like structure with the presence of sharp and intense peaks at low angle values as well as less intense peaks at higher values of 2θ. Figure 2 revealed the XRD patterns of Mg-Al mixed oxides prepared by calcination of Mg-Al LDH. It was found that the layered crystalline structure of Mg-Al LDH was destroyed during calcination. The results indicated that all samples have MgO-like structure since the incorporation of smaller Al$^{3+}$ cations into the bulk lattice to form a solid solution. Furthermore, their peak intensities increased with the Mg/Al molar ratio increasing.
3.2. Catalytic performance

Catalytic properties of Mg-Al mixed oxides with different Mg/Al molar ratios were evaluated by the transesterification of DMC with DEC at first. As shown in Table 1, MgAlO-3-600 performed the highest activity among the Mg-Al mixed oxides, whereas MgAlO-6-600 showed the lowest activity. The catalytic activity of various Mg-Al mixed oxides increased in the order MgAlO-6-600 < MgAlO-4-600 < MgAlO-2-600 < MgAlO-5-600 < MgAlO-3-600. According to the results of previous literatures, there is a good correlation between the surface basic density of Mg-Al mixed oxides and their catalytic activity in the transesterification [1]. It is well known that the basic property of Mg-Al mixed oxides depends not only on the Mg/Al molar ratio but also on the calcination temperature. Thus, the effect of roasting temperature on the activity of Mg-Al mixed oxides was also studied. The calcination temperature of LDH must be high enough to form porous mixed oxides with relatively high surface area, but it could not exceed a critical temperature in order to avoid phase segregation and sintering. Therefore, the calcination temperature for MgAlO-3-T (T: calcination temperature) was ranged from 400°C to 700°C in the present work. As shown in Table 1, the EMC yield quickly raised from 26.9% to 51.6% with increasing the calcination temperature from 400°C to 600°C using MgAlO-3-600 as catalyst. However, EMC yield quickly decreased from 51.6% to 33.7% with further rising the calcination temperature to 700°C. According to above results, the optimum calcination temperature was 600°C for MgAlO-3-T.

Figure 1. XRD spectrums of Mg-Al LDH with different Mg/Al molar ratio

Figure 2. XRD spectrums of Mg-Al mixed oxides with different Mg/Al molar ratio
| Entry | Catalyst       | Yield (%) |
|-------|----------------|-----------|
| 1     | MgAlO-2-600    | 35.6      |
| 2     | MgAlO-3-600    | 51.6      |
| 3     | MgAlO-4-600    | 26.5      |
| 4     | MgAlO-5-600    | 39.3      |
| 5     | MgAlO-6-600    | 19.2      |
| 6     | MgAlO-3-400    | 26.9      |
| 7     | MgAlO-3-500    | 40.1      |
| 8     | MgAlO-3-700    | 33.7      |

Reaction condition: DMC (9.00 g, 100 mmol), DEC (11.80 g, 100 mmol), catalyst (1 wt%, based on the total material), 100°C, 1.5 h.

3.3. Reusability of catalyst
The reusability is one of key indexes for heterogeneous catalysts. Therefore, the reusability test of MgAlO-3-600 was investigated in the presence of 1 wt% MgAlO-3-600 at 100°C in 1.5 h. After the reaction, MgAlO-3-600 was filtered, washed and dried with ethanol. And then MgAlO-3-600 was used for the next run of EMC synthesis. As shown in Figure 3, MgAlO-3-600 could be reused for the EMC synthesis from DEC and DMC in 4 runs without obviously change of its catalytic activity. In addition, the selectivity of EMC was almost nearly 100% for all runs studied. Above results indicated that MgAlO-3-600 performed well reusability.

![Figure 3. Reusability of MgAlO-3-600 for the synthesis of EMC](image)

3.4. Comparison with other reference catalysts
The activity of MgAlO-3-600 was compared with other reported catalysts for the synthesis of EMC from DMC and DEC, and the results were listed in Table 2. Obviously, MgAlO-3-600 showed higher activity than other representative heterogeneous catalysts reported by previous literatures [1–4]. And MgAlO-3-600 gave the highest turnover frequency (TOF) value with highest EMC yield under similar reaction conditions, indicating that MgAlO-3-600 could be used as efficient heterogeneous catalyst for the synthesis of EMC.

| Catalyst        | Amount of catalyst (%) | Time (h) | Yield (%) | TOF b | Reference |
|-----------------|------------------------|----------|-----------|-------|-----------|
| MgAlO-3-600     | 1.0                    | 1.5      | 51.6      | 165.4 | This work |
| MgAlO_4        | 4.8                    | 0.5      | 49        | 98    | [1]       |
4. Results and discussion

The composition, structure and catalytic property of Mg-Al mixed oxides can be tailored by simple change of Mg/Al molar ratio and/or roasting temperature for the EMC synthesis. Among the studied catalysts, MgAlO-3-600 shows the highest activity. And 51.6% EMC yield can be obtained by using 1% MgAlO-3-600 as catalyst at 100°C in 1.5 h. In addition, MgAlO-3-600 can be reused in the title reaction at least 4 times without obviously change of its catalytic activity.

Acknowledgments

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