

Layered Hydroxide Catalysts for Transesterification of Tributyrin with Methanol

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Introduction

Solid base catalysts are potentially useful in the production of fuels and chemicals. Because solid bases are easily separated from reaction media, they are attractive alternatives to traditional homogeneous base catalysts that require complicated downstream separation and neutralization processes [1,2].

Hydrotalcite (HT) is a layered double hydroxide with the general formula of $[Mg_{1-x}Al_x(OH)_2]^{x+}(CO_3)_{x/2} \cdot nH_2O$. The decomposition of HT generates a high surface area Mg-Al mixed oxide that exposes a variety of base sites on the solid surface. Interestingly, reconstruction of the layered HT from a decomposed sample by exposure to water generates Brønsted base sites between the new layers that exhibit enhanced activity [3]. In addition, rare-earth hydroxynitrate, such as $Y_2(OH)_5NO_3 \cdot nH_2O$ (YHN), is another class of layered materials [4]. The positively charged layer is composed of trivalent rare-earth metal hydroxocations, which are capable of coordinating to a variety of anions. Organic anions that are intercalated into yttrium hydroxides have possible applications in green chemical synthesis and heterogeneous catalysis [4,5].

In this work, the catalytic activity of activated HT and intercalated yttrium hydroxide was evaluated in the transesterification of tributyrin with methanol, a model reaction for biodiesel production [6]. The influences of HT activation procedure, interlayer water removal and crystallinity of the reconstructed HT were studied. In addition, ethylene glycoxide anion ($O-CH_2-CH_2-O^-$) was intercalated into layered yttrium hydroxide and tested as a catalyst for transesterification.

Materials and Methods

The Mg-Al HTs were prepared by coprecipitation or by hydrothermal synthesis involving urea hydrolysis [7], denoted as CHT and UHT, respectively. The synthetic Mg-Al HTs were activated by either thermal decomposition (723 K, $100\text{ cm}^3\text{ min}^{-1}\text{ N}_2$, 8 h), denoted as CHT-d or UHT-d, or thermal decomposition followed by reconstruction. The hydrothermally reconstructed HTs were denoted as CHT-d-rl or UHT-d-rl, whereas the gas phase reconstructed CHT-d sample was denoted as CHT-d-rg. The transesterification reaction was performed in a batch reactor equipped with a reflux condenser and with methanol to tributyrin molar ratio of 30:1 at 333 K.

The YHN sample was prepared by a hydrothermal synthesis method [4]. The intercalation of ethylene glycoxide anion into YHN was accomplished by heating a mixture of YHN, ethylene glycol and 0.5 M sodium methoxide solution in methanol at 413 K for 20 h.

Results and Discussion

The reconstructed HTs were significantly more active than the decomposed HTs on a surface area basis. The areal reaction rate and CO_2 adsorption capacity of the reconstructed sample decrease significantly as the interlayer water was removed by thermal treatment. The catalytic activity of reconstructed HTs had the order of $CHT-d-rg \gg UHT-d-rl > CHT-d-rl$, which is opposite of the trend in crystallinity, suggesting the importance of crystal edges and defects in activity. Both the decomposed and reconstructed HT samples deactivated during the transesterification reaction. The crystal structure of decomposed HT was stable under reaction condition as shown in Figure 1(b) and (d). However, the Brønsted base sites of the reconstructed HT were deactivated by the hydrolysis side reaction, resulting in the formation of the butyric acid anion and expansion of interlayer distance illustrated by comparing the diffraction patterns in Figure 1(c) and (e). The intercalation of ethylene glycoxide anion into YHN was also accomplished in this work. The ethylene glycoxide loaded YHN exhibited similar catalytic activity for transesterification of tributyrin with methanol to the reconstructed HTs.

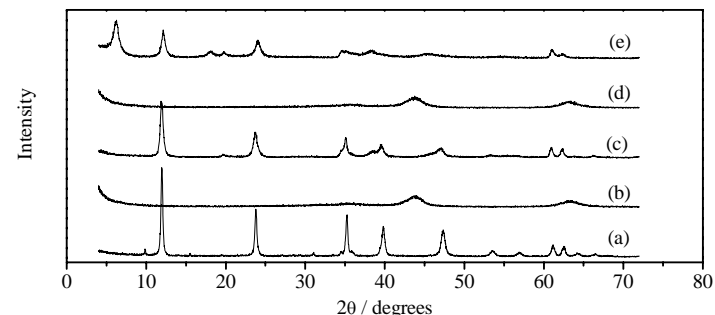


Figure 1. XRD patterns of (a) UHT, (b) UHT-d, (c) UHT-d-rl, (d) recycled UHT-d after 2 runs, (e) recycled UHT-d-rl after 2 runs.

Significance

The main goal of this work is to understand the fundamental nature of solid base catalysts that could potentially replace the homogeneous bases currently used in the production of biodiesel fuel.

References

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