

Tunable transesterification of dimethyl carbonate with ethanol on K_2CO_3/Al_2O_3 catalysts: Study on the mechanism and kinetics

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Highlights

- The active sites of prepared K_2CO_3/Al_2O_3 catalysts for the transesterification reaction was studied.
- An efficient catalyst system could be performed stably over 2000 h.
- The kinetic modeling and reaction mechanism of the transesterification reaction were revealed.

1. Introduction

Organic carbonates, such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), et al. are indispensable co-solvents of lithium battery electrolyte [1,2]. With the rapid development of lithium ion battery and other energy shortage systems, more than one million tons of high-purity of these carbonates are needed annually with a great increase in demand in recent years. Among these carbonates, EMC and DEC are worthy of special concerns, which are produced from the transesterification of DMC and ethanol, under the mild reaction conditions [3,4]. Nevertheless, the commercial production of EMC and DEC faces great challenges in the catalysts with high catalytic activity and high stability [5]. In this work, a novel solid-base catalyst with varied active sites of $KAl(OH)_2CO_3$, K_2CO_3 , and $KAlO_2$ was studied systematically. A rational reaction mechanism and kinetics were proposed.

2. Methods

The K-based solid base catalysts were prepared via an incipient wetness impregnation method, with potassium hydrogen carbonate ($KHCO_3$) used as the precursor of potassium species. The transesterification of DMC with ethanol was performed in a U-shaped fixed-bed reactor equipped with a vaporizer. All the products were analysed on-line by a GC with an FID detector.

3. Results and discussion

The transesterification reaction of DMC with ethanol was first tested on the prepared $K_2CO_3/\gamma-Al_2O_3$ catalysts calcined at 400 °C. As shown in Fig. 1A, DMC conversion increased first and then decreased with the increase of K_2CO_3 contents with the highest at $15K_2CO_3/\gamma-Al_2O_3$. The satisfactory activity of the prepared $K_2CO_3/\gamma-Al_2O_3$ catalyst was supposed to be related with the synergistic effect of K_2CO_3 and $\gamma-Al_2O_3$, and depends on the calcination temperature obviously. The K_2CO_3/Al_2O_3 catalyst calcined at 200 °C with the active sites of $KAl(OH)_2CO_3$ displayed the highest activity, while the activity of the catalyst decreased with the increase of calcination temperature (Fig. 1B), due to formation of the active species of K_2CO_3 and $KAlO_2$. However, the catalyst calcined at 400 °C displayed the active sites of K_2CO_3 and $KAlO_2$ species and showed a superior stability with a test duration over 2000 hours of little change in the performance (Fig. 1C).

A rational catalytic mechanism of $K_2CO_3/\gamma-Al_2O_3$ for the transesterification reaction was proposed (Fig. 2A), with three types reactions carried out simultaneously: (I) dissociative adsorption, (II) nucleophilic addition and substitution, (III) catalyst cycle. A dissociative adsorption of ethanol and DMC was conducted on the catalyst surface. Then, a nucleophilic addition and substitution reaction takes place between the adsorbed $EtO^{\delta-}$ species and $COOCH_3^{\delta+}$ species to form new carbonate products. The formed methanol is desorbed from the catalyst to regenerate the active sites. The corresponding kinetic model by the nonlinear regression was presented in Fig. 2B, which demonstrated an excellent agreement between the experimental and calculated results. The estimated apparent activation energies for reaction

R1 and R2 are 34.09 kJ/mol and 33.60 kJ/mol respectively, implying the two consecutive reactions occurring on a similar rate determining step.

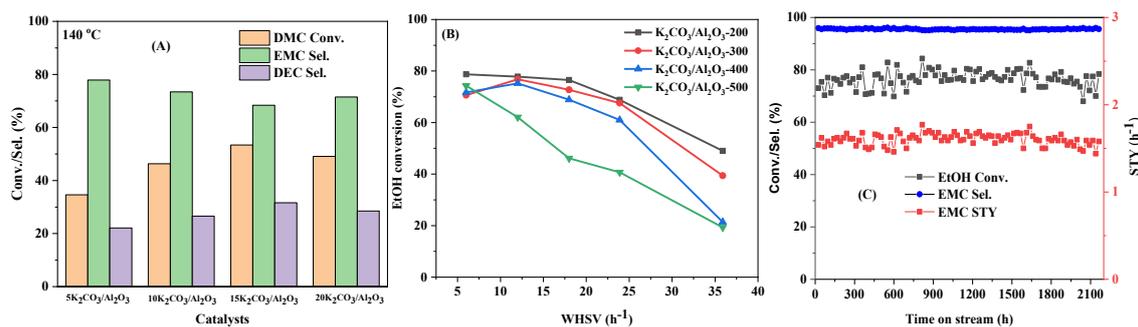


Figure 1. The catalytic performance of prepared K_2CO_3/Al_2O_3 catalysts: (A) the effect of K_2CO_3 loading, (B) the effect of calcined temperature, (C) the stability test of the K_2CO_3/Al_2O_3 -400 catalyst.

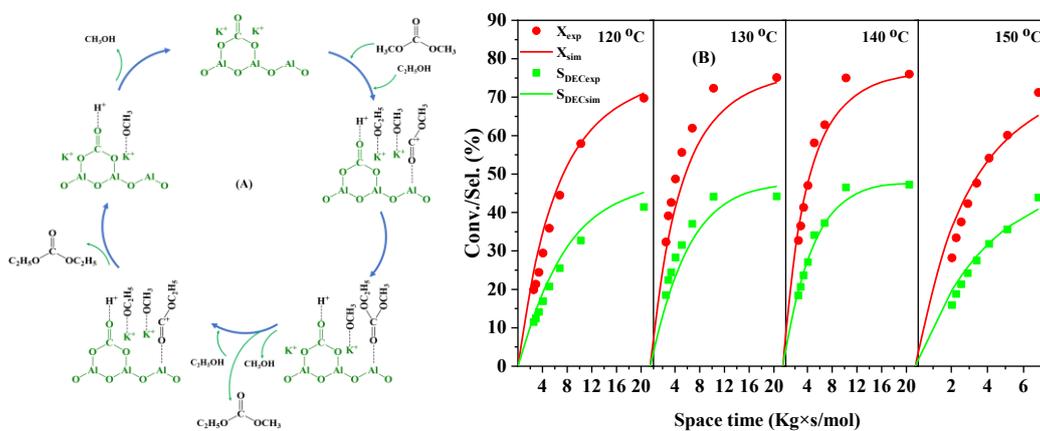


Figure 2. (A) The proposed catalytic mechanism of K_2CO_3/Al_2O_3 for the transesterification reaction, (B) the kinetic model.

4. Conclusions

A K_2CO_3/Al_2O_3 catalyst system with high catalytic performance and stability was established. The active sites of $KAl(OH)_2CO_3$ on K_2CO_3/Al_2O_3 showed high activity for the transesterification reaction, while that of K_2CO_3 and $KAlO_2$ displayed superior stability. The mechanism for the two consecutive reactions was proposed, which includes three elemental reactions of dissociative adsorption, nucleophilic addition and substitution, and catalyst cycle. A kinetic model with the apparent activation energies of 34.09 kJ/mol and 33.60 kJ/mol respectively was obtained.

References

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Keywords

Transesterification; Solid base; K_2CO_3 ; Kinetic model.